

## Supporting Information

# Cosolvent-Promoted O-Benzylation with Silver(I) Oxide: Synthesis of 1'-Benzylated Sucrose Derivatives, Mechanistic Studies, and Scope Investigation

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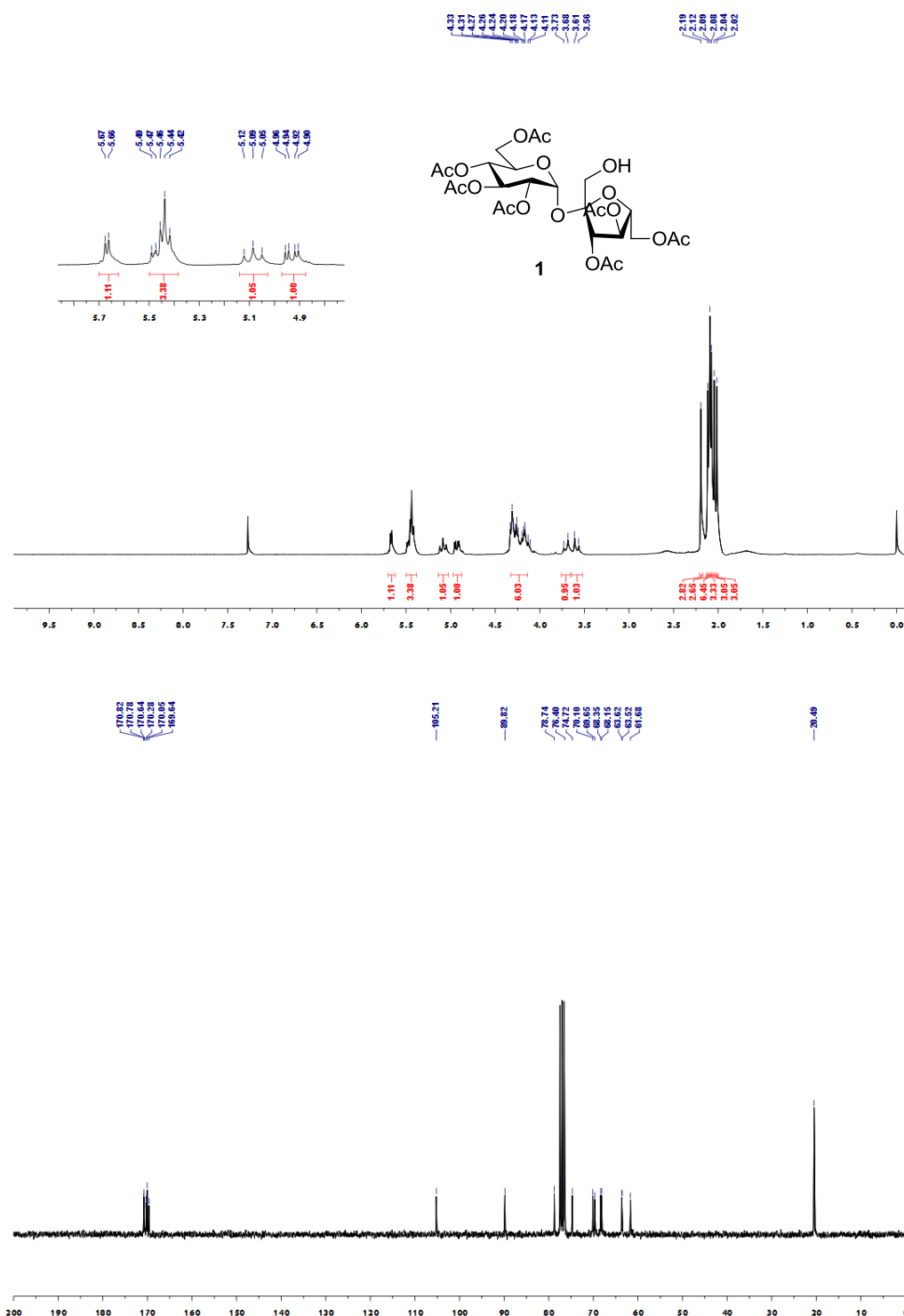
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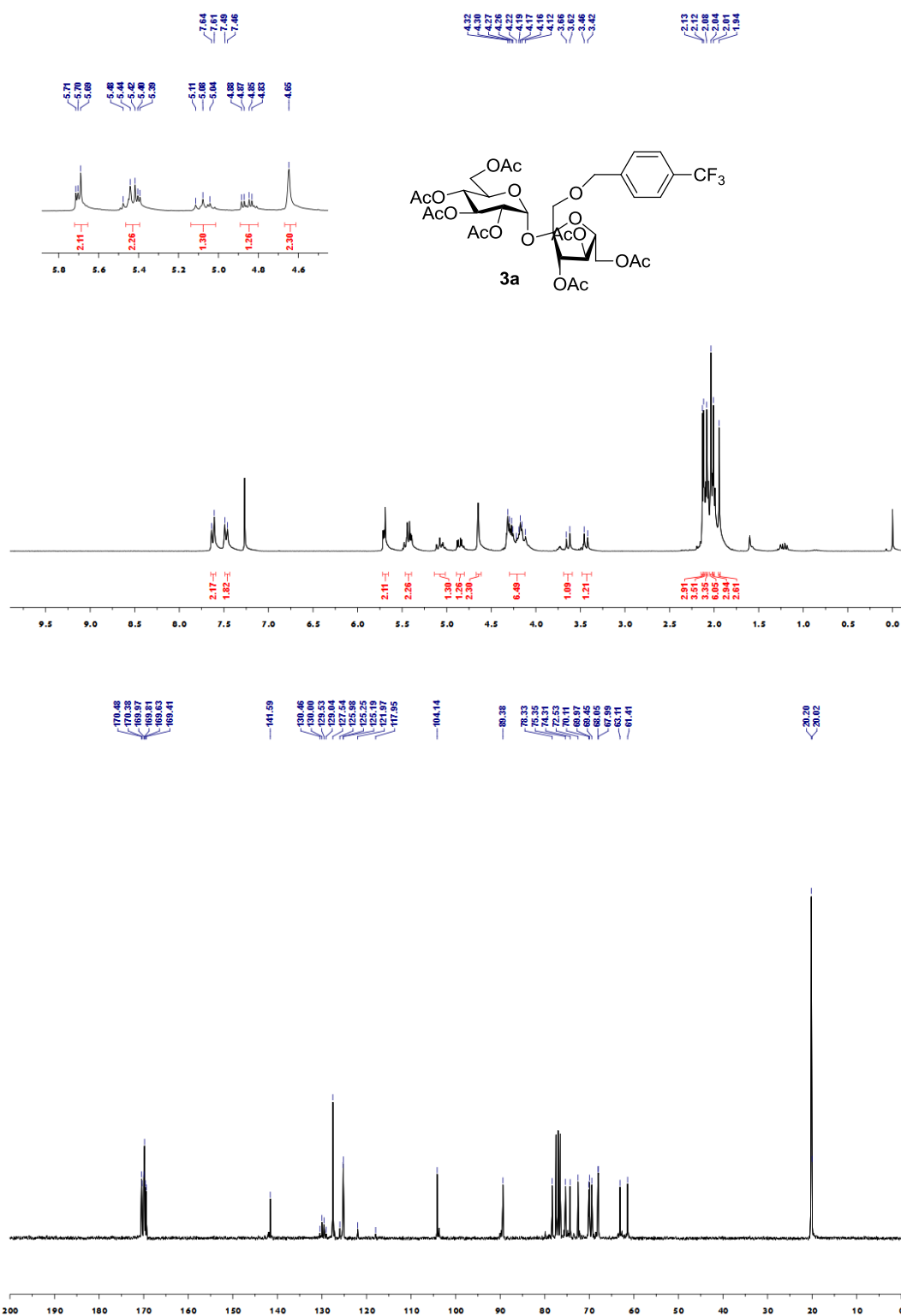
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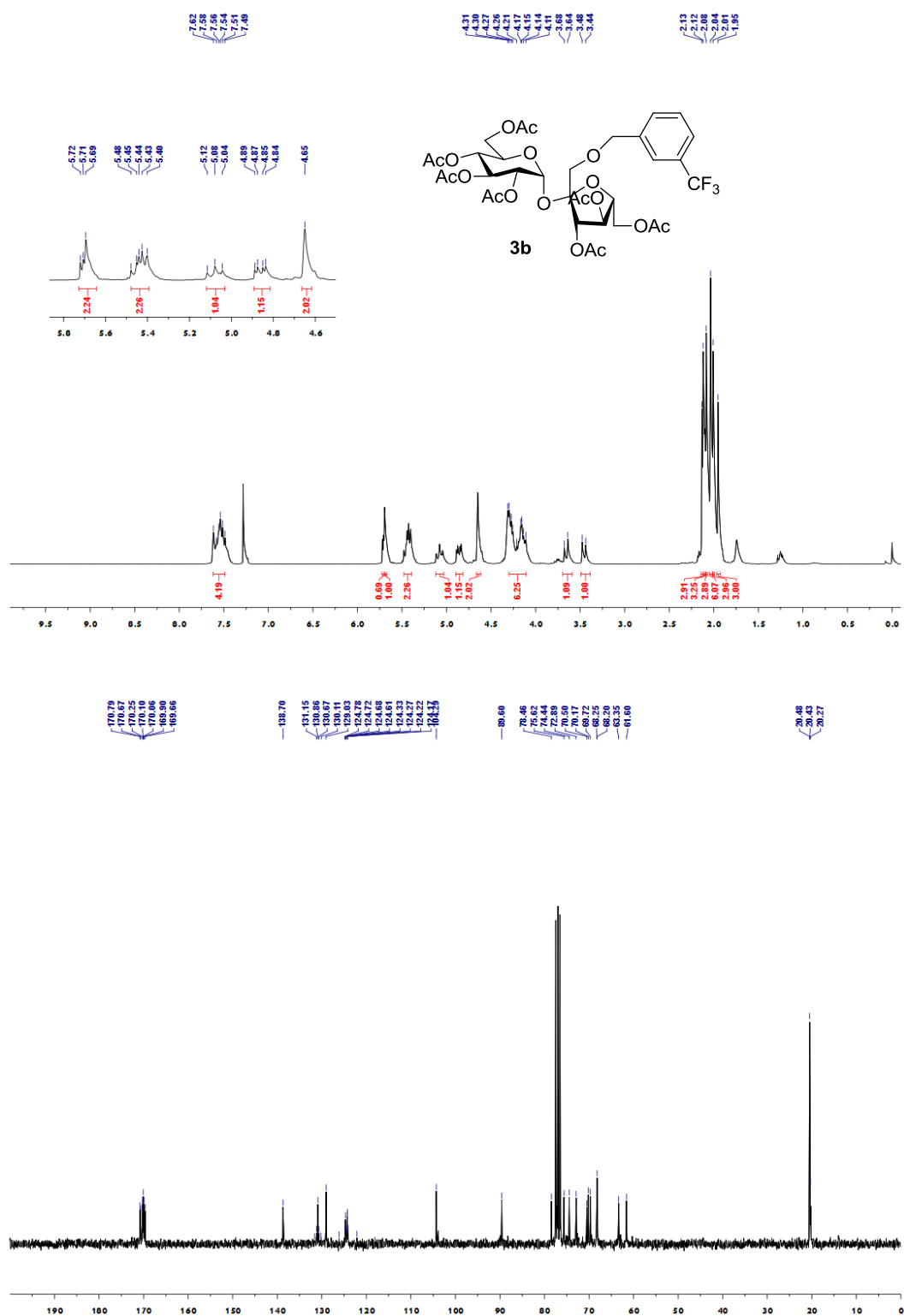
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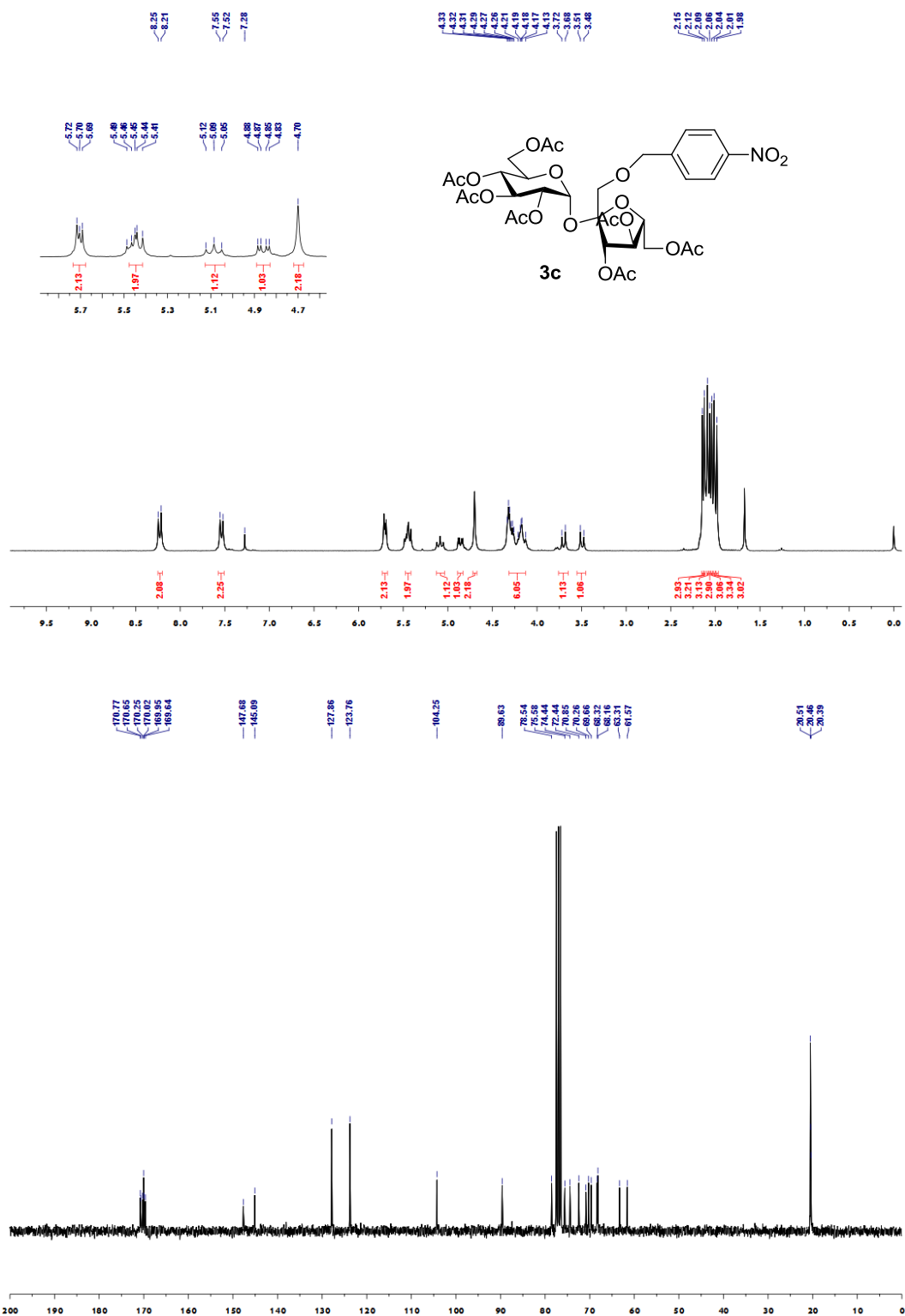
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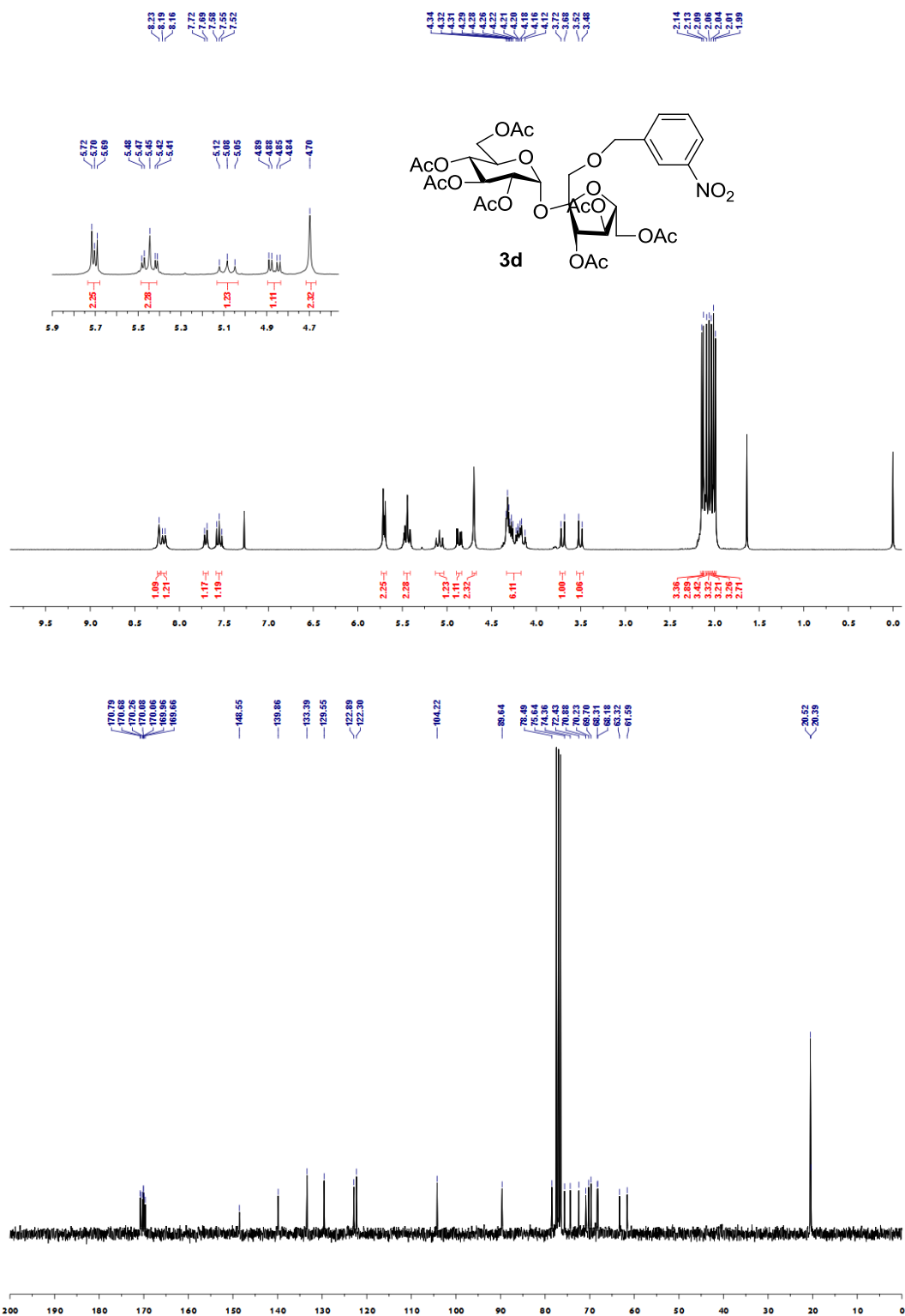
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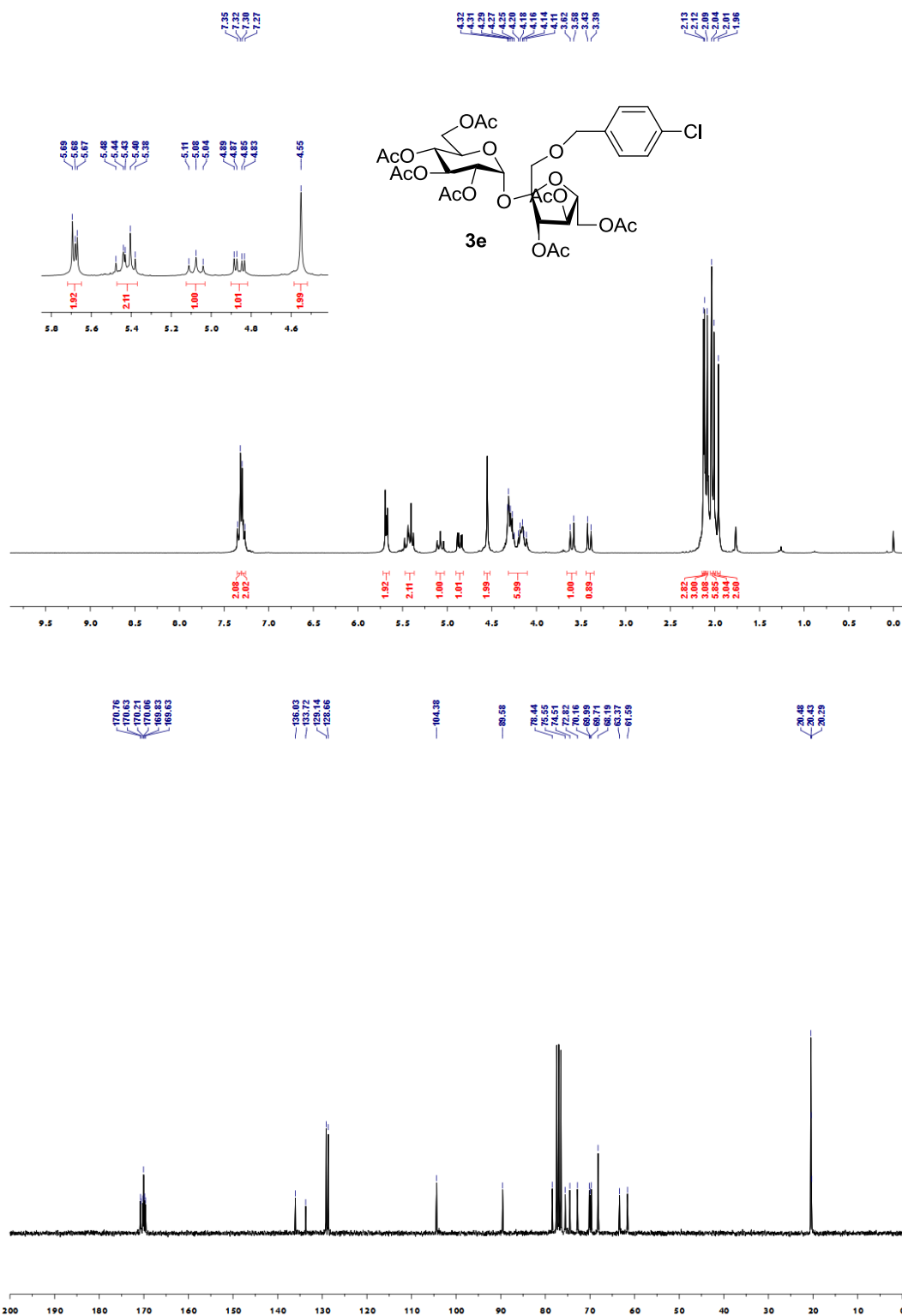


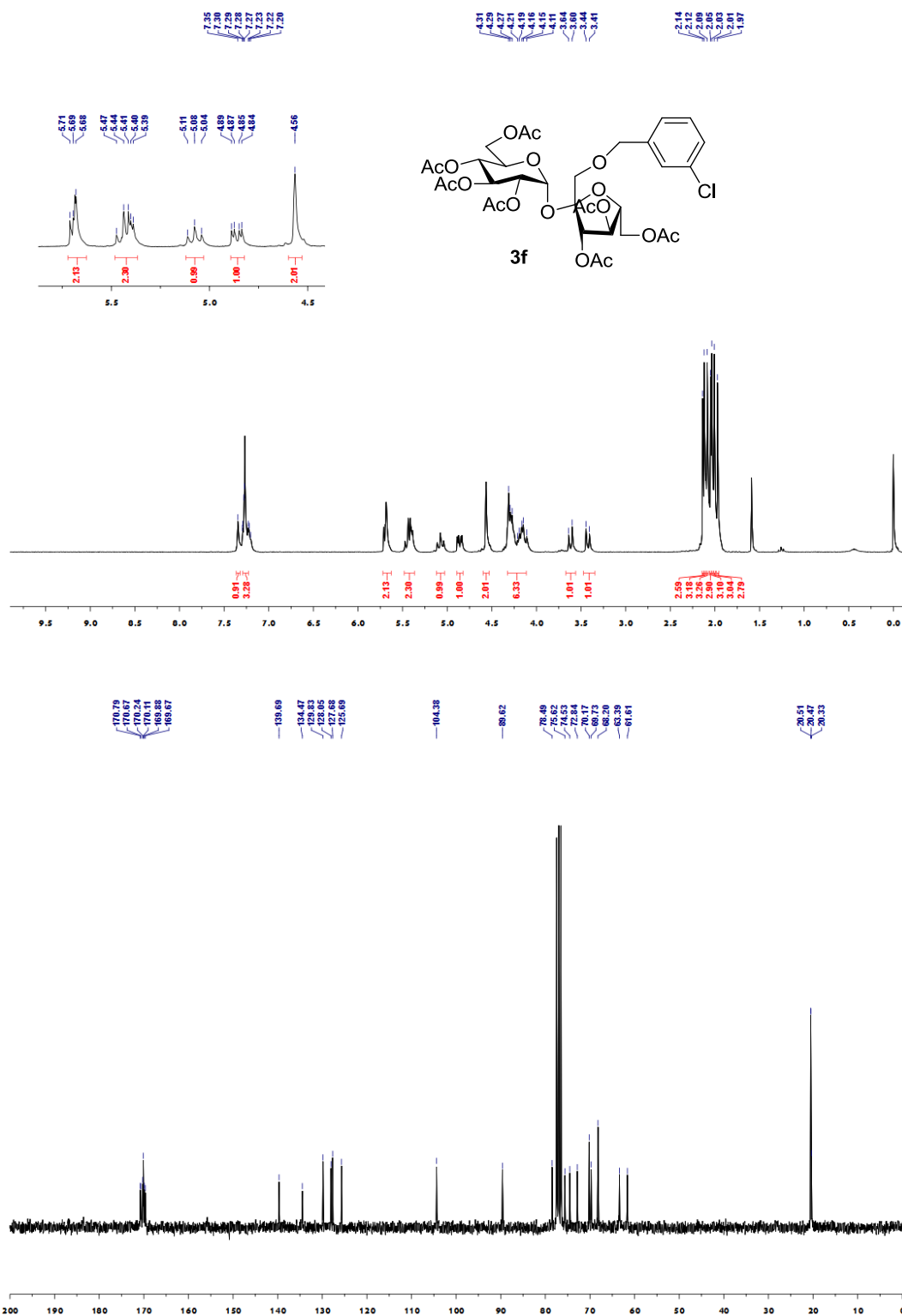




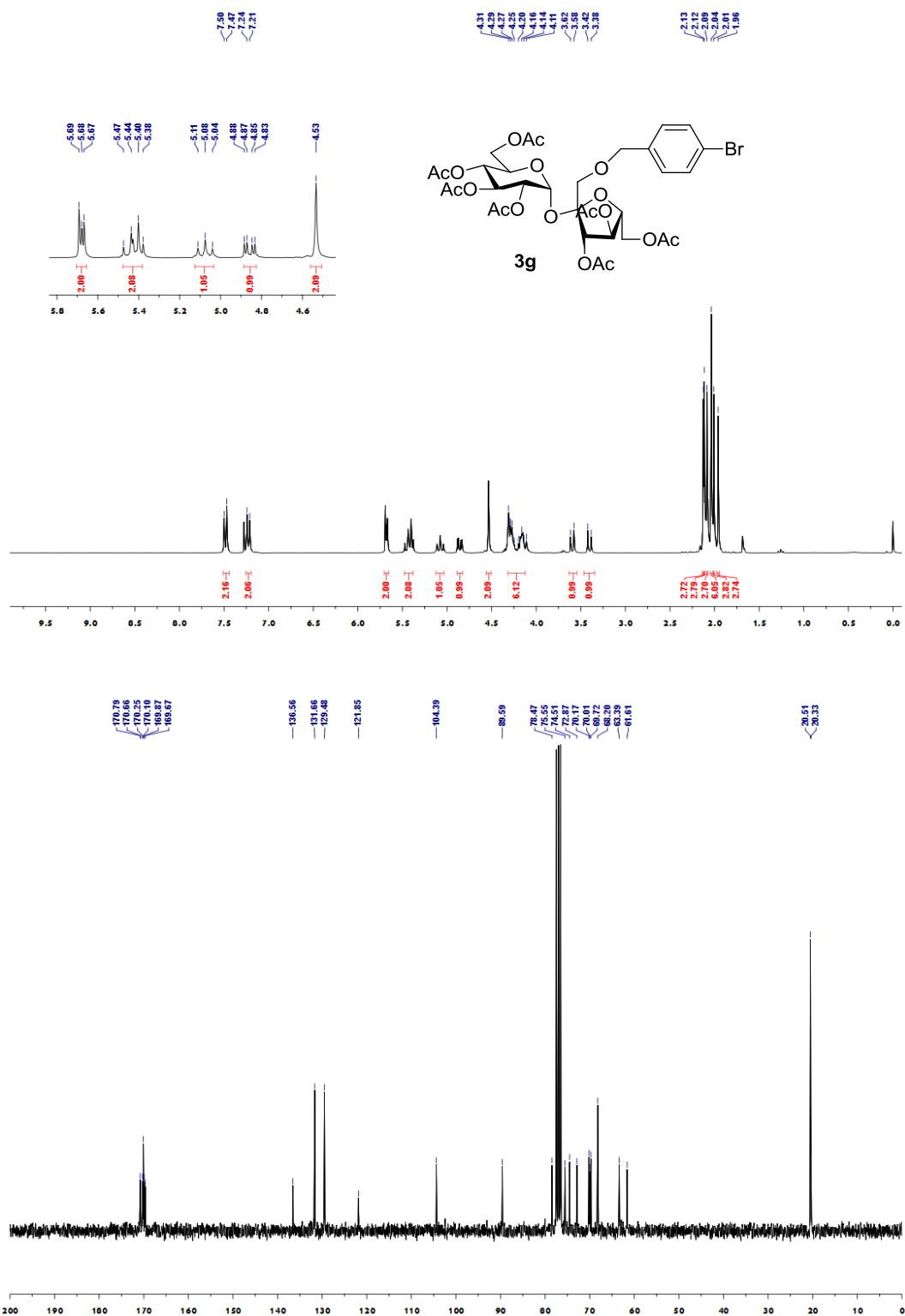


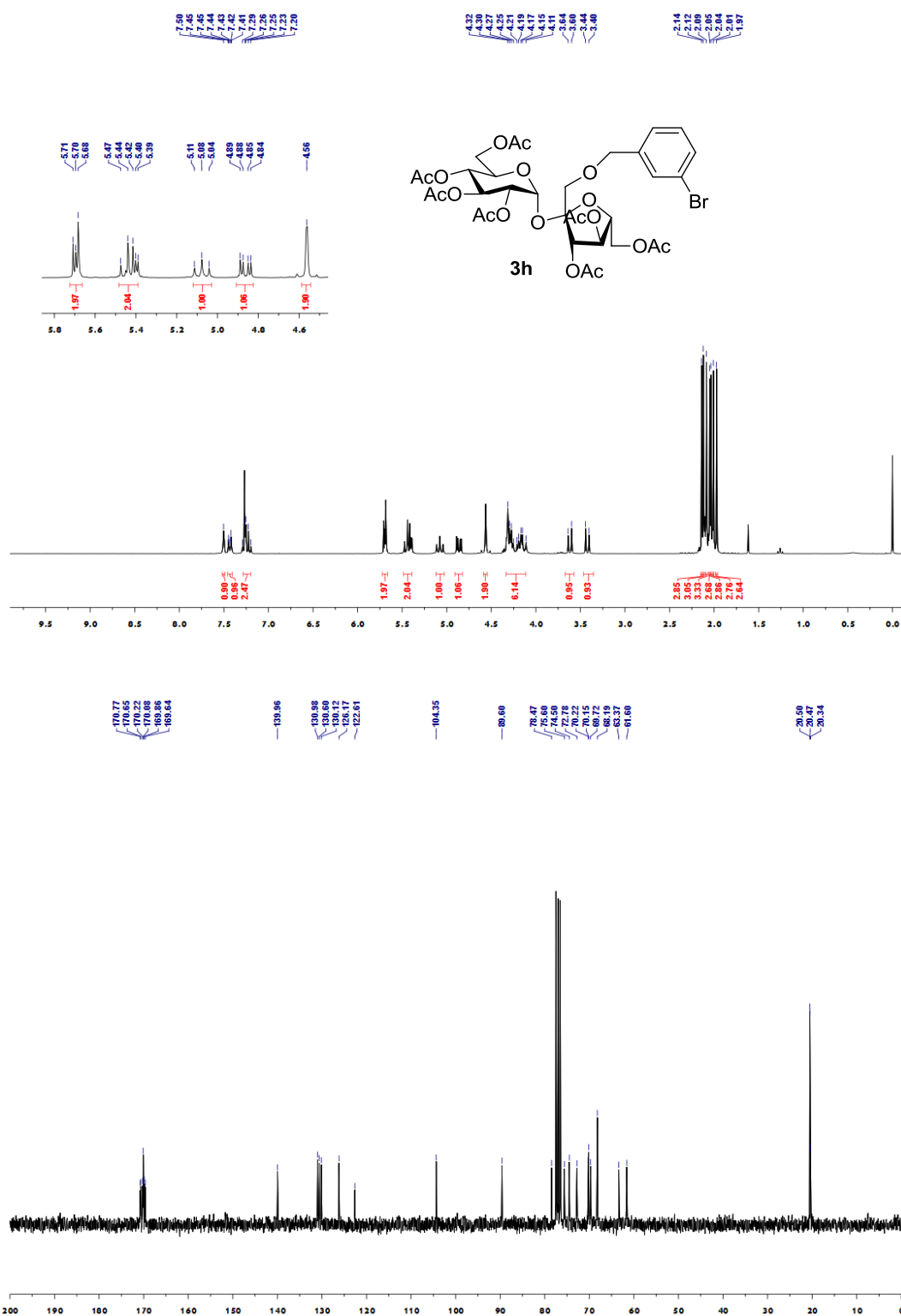


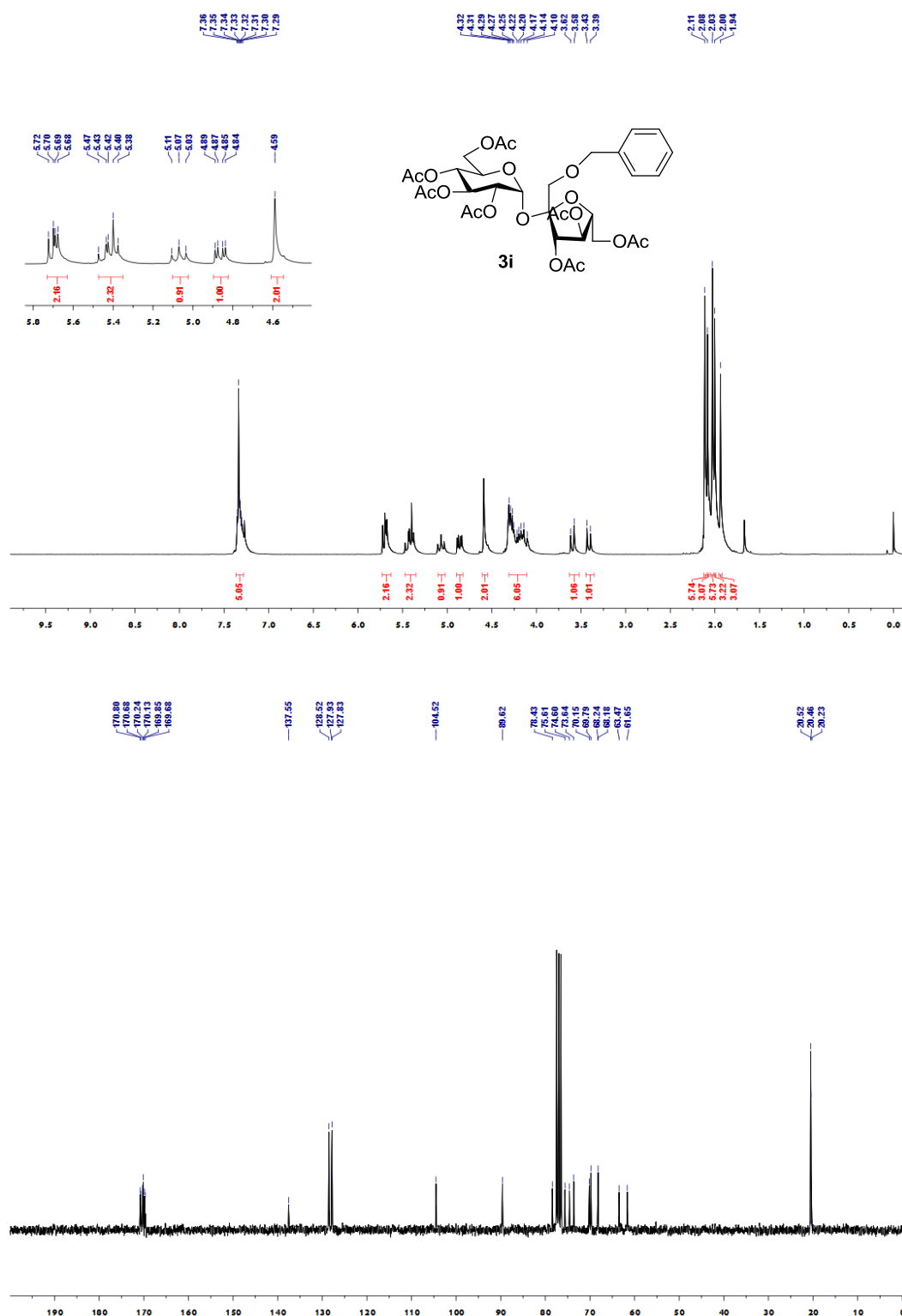


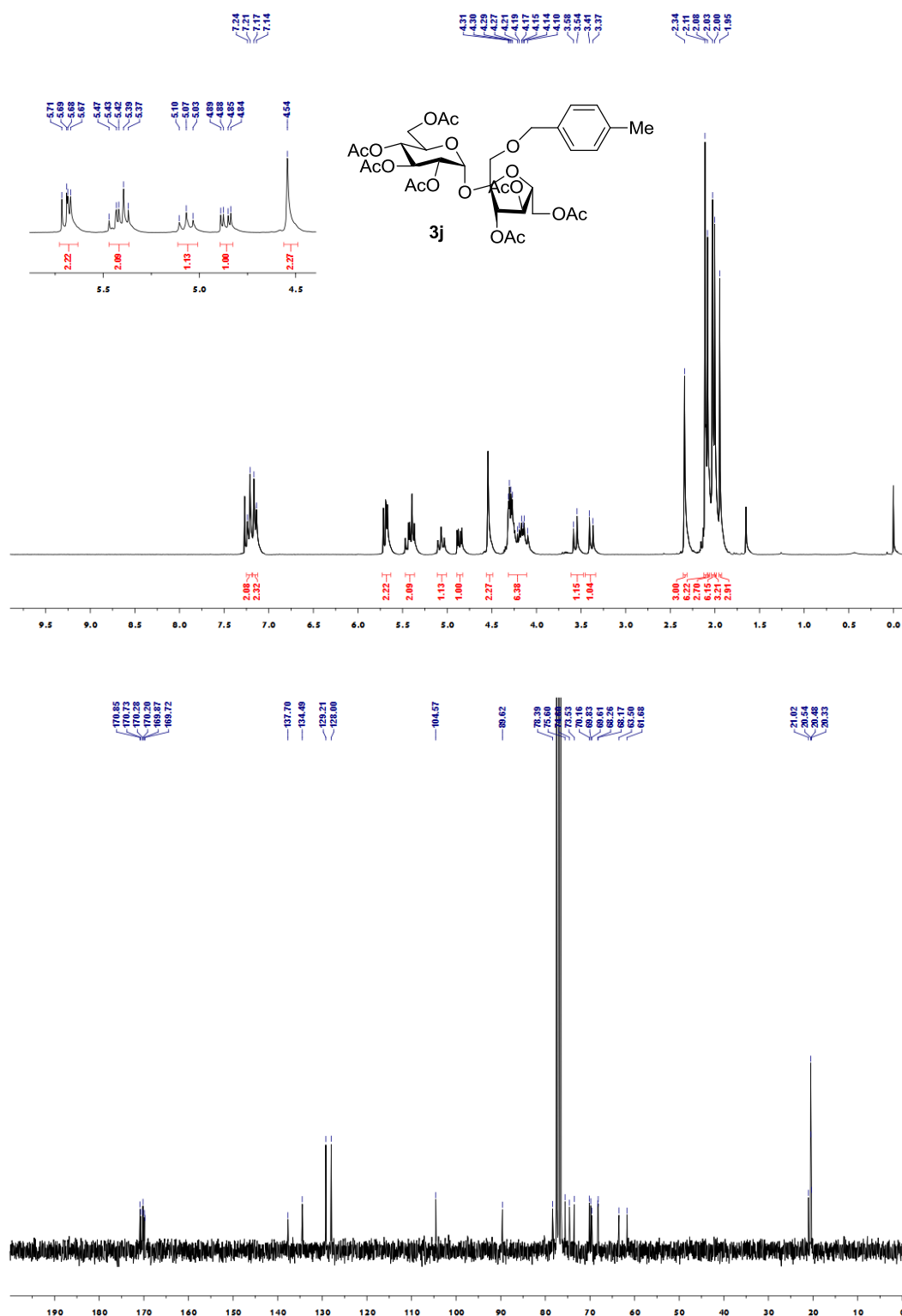


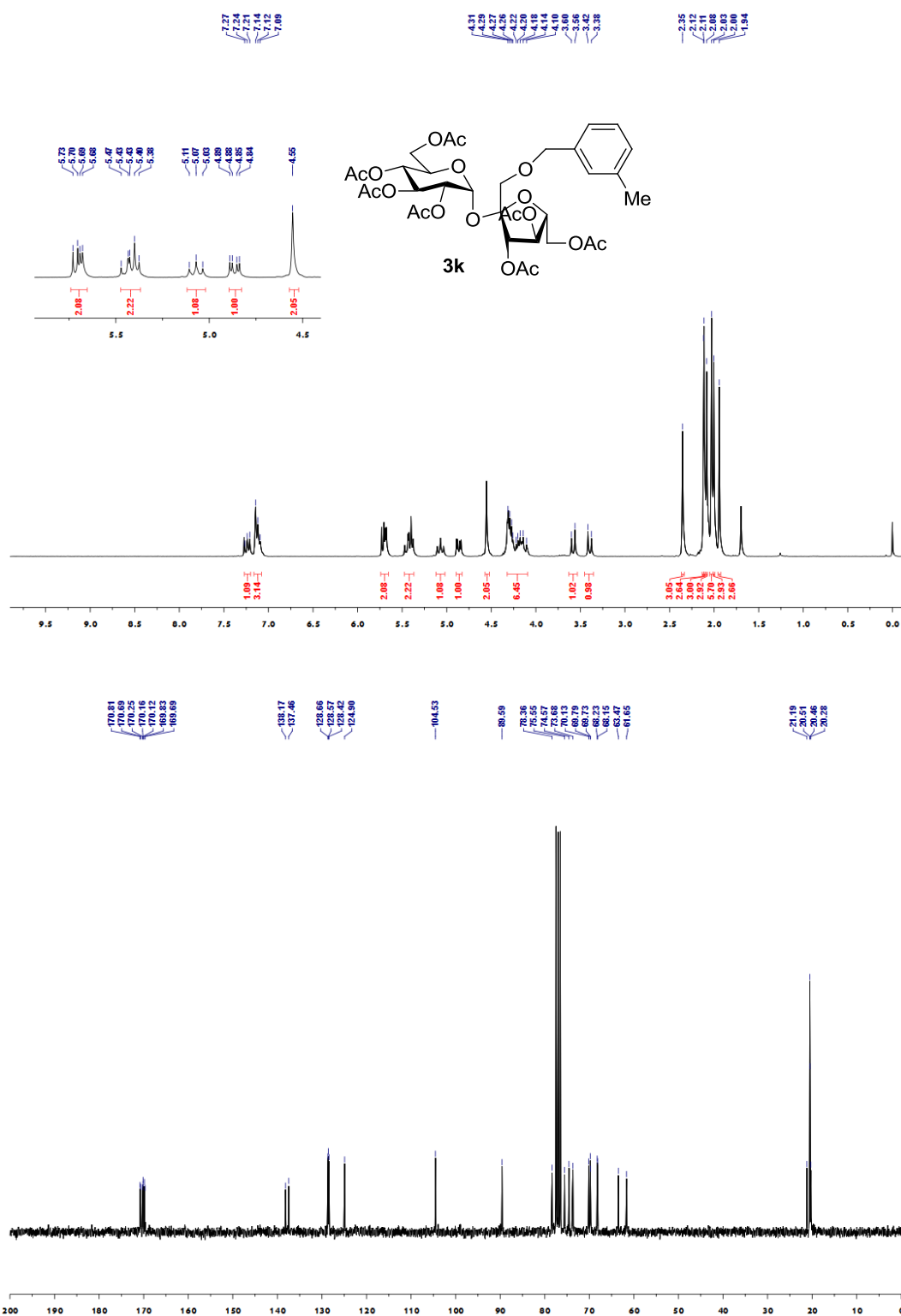


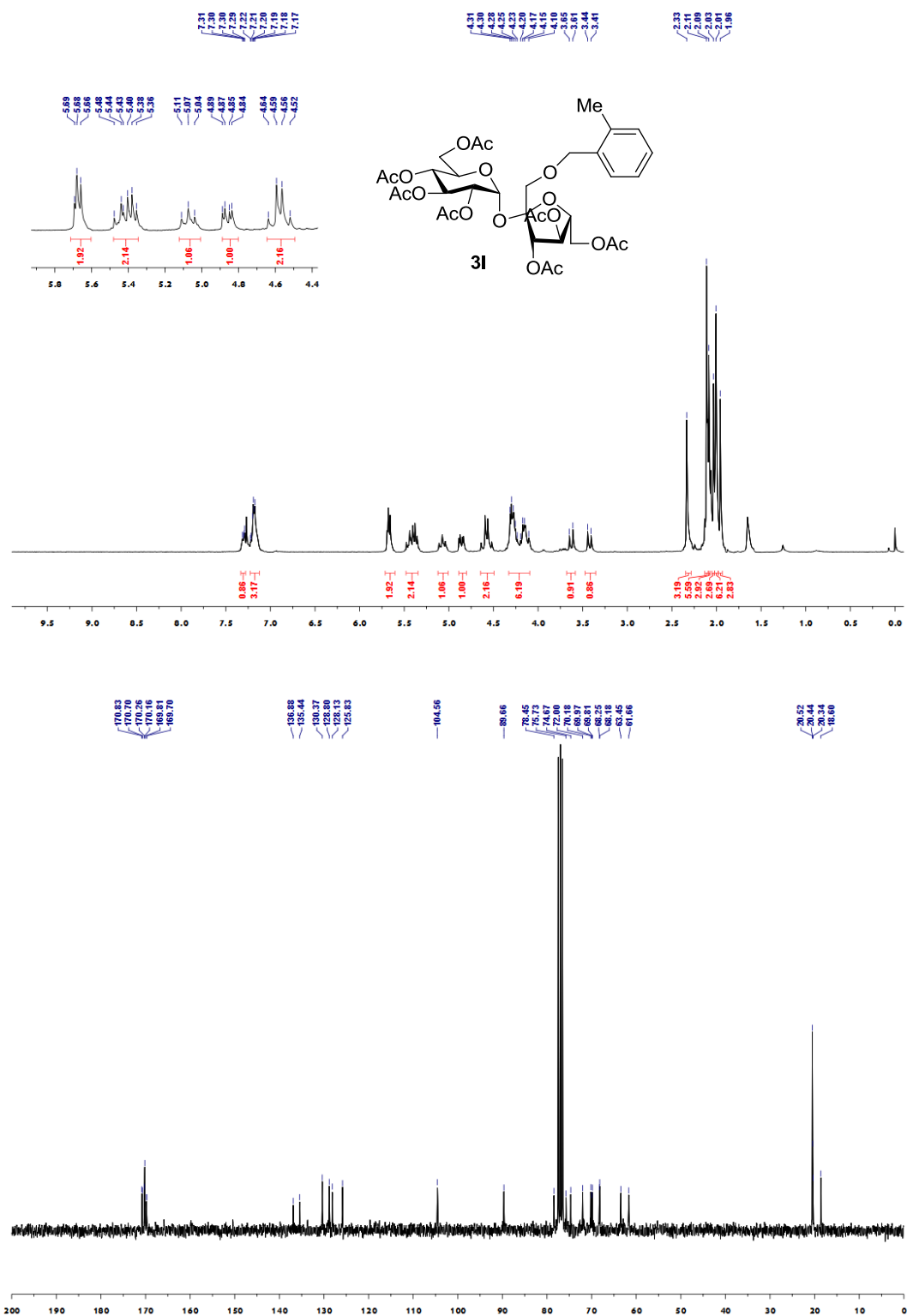


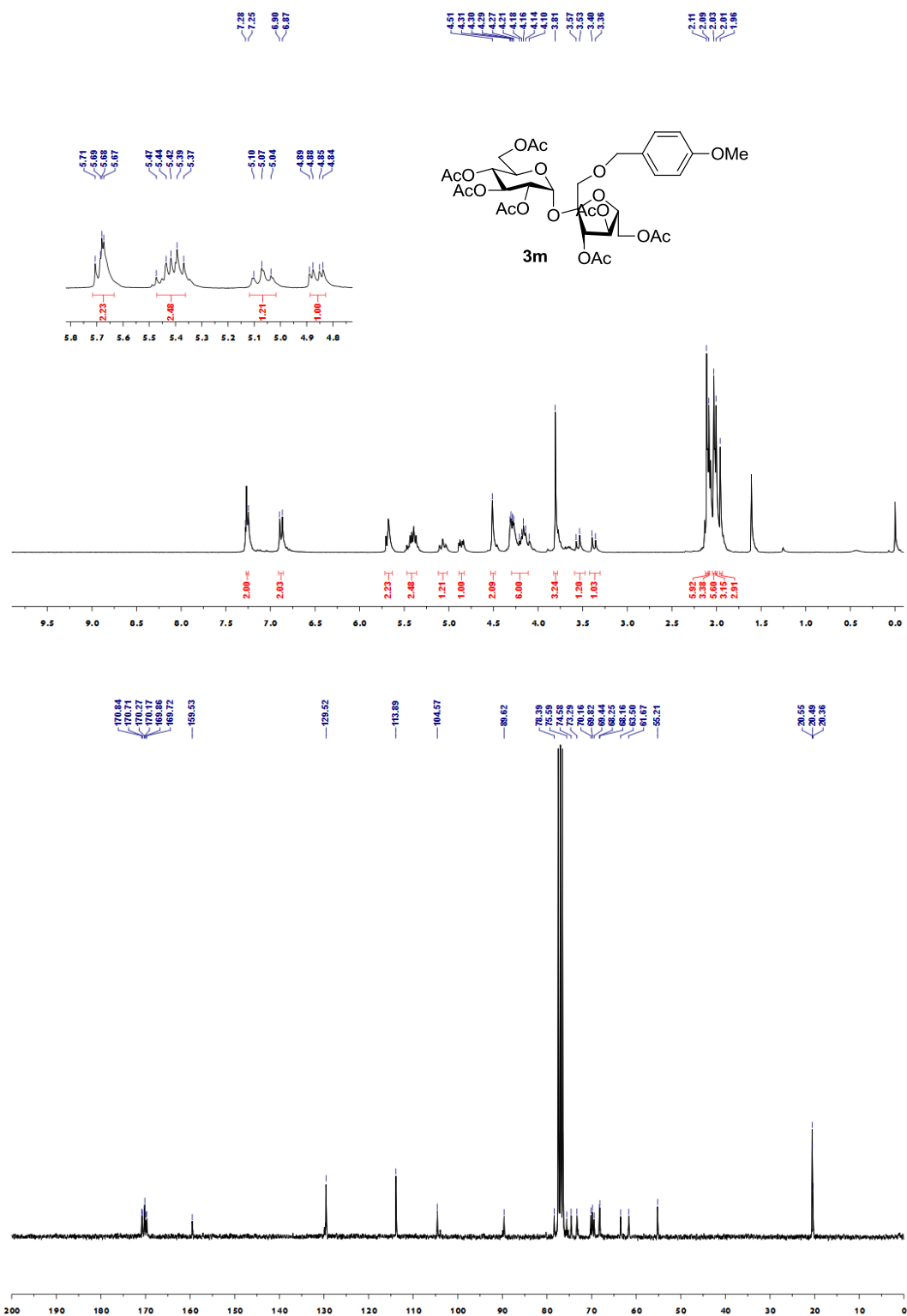


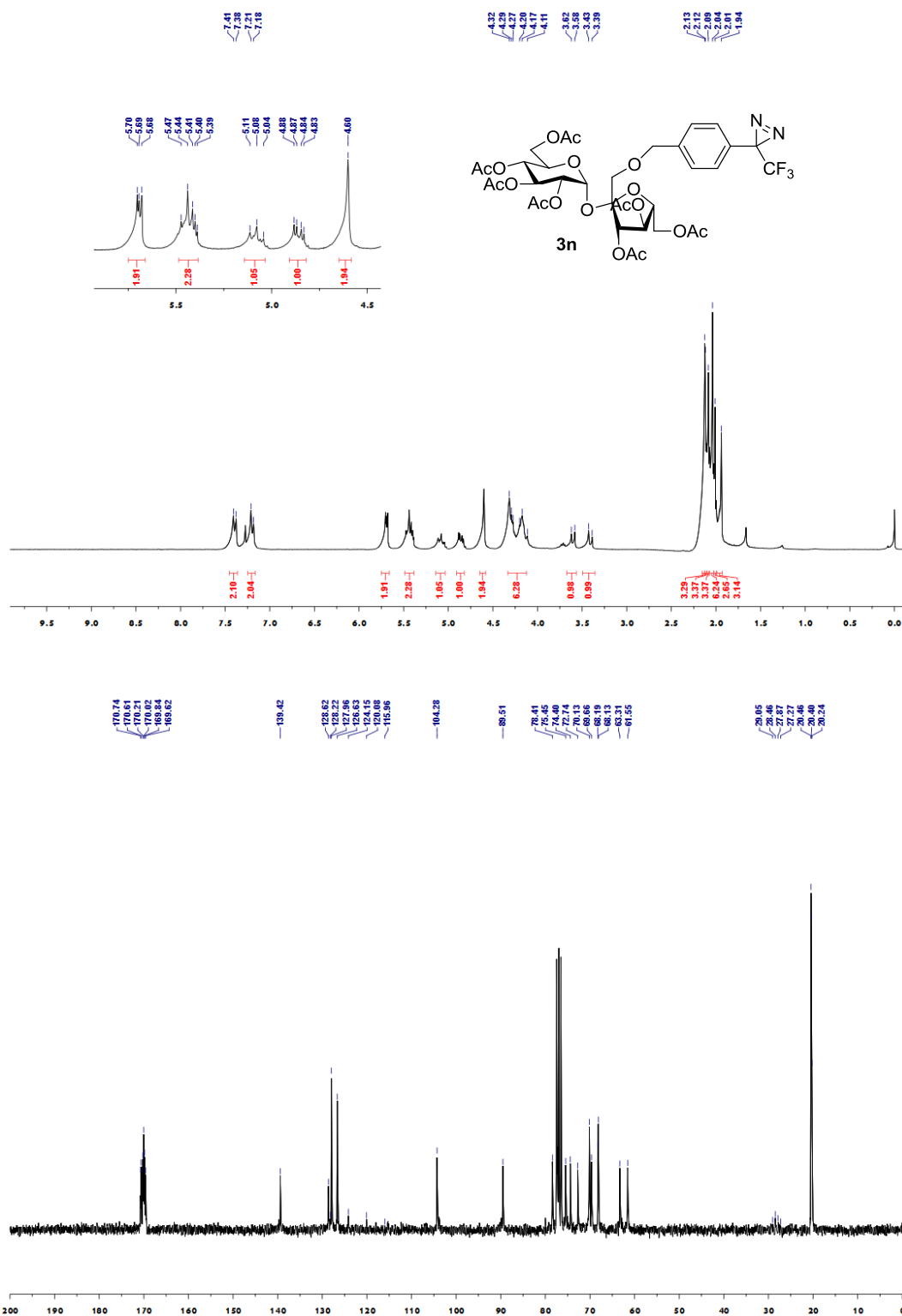




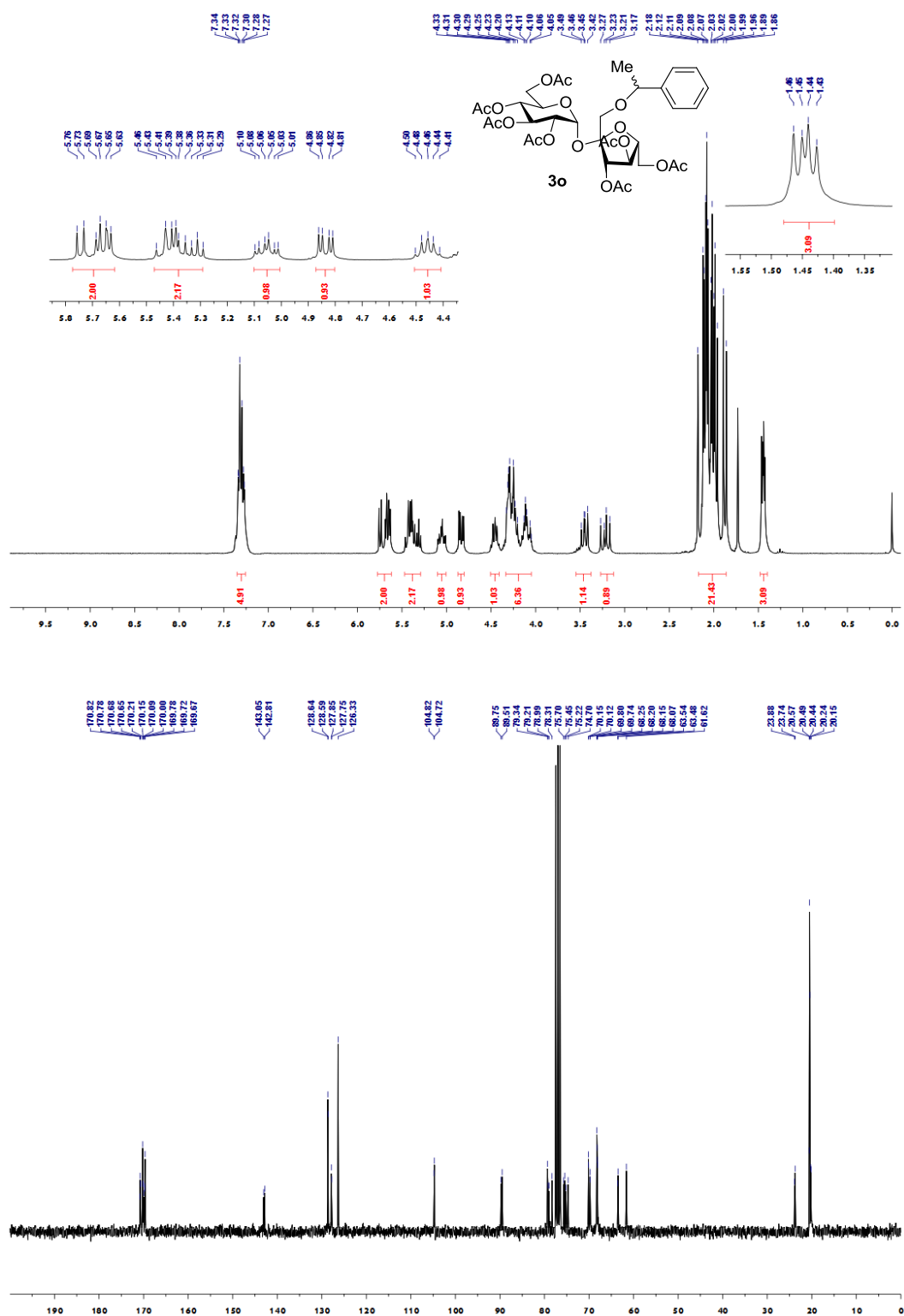


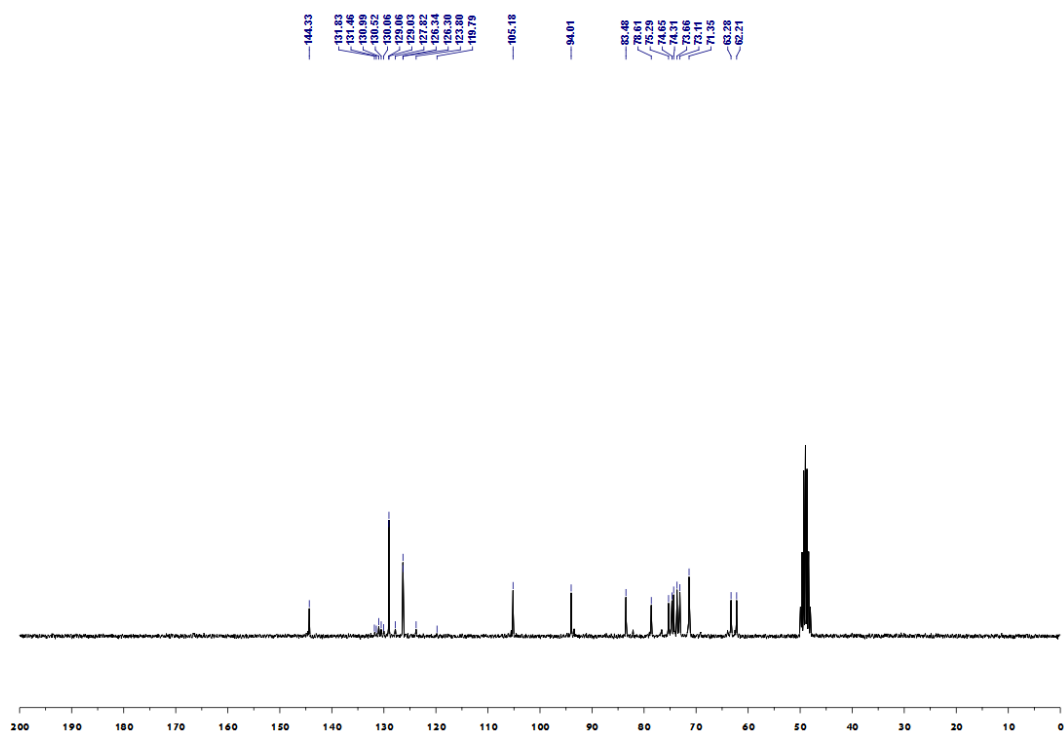
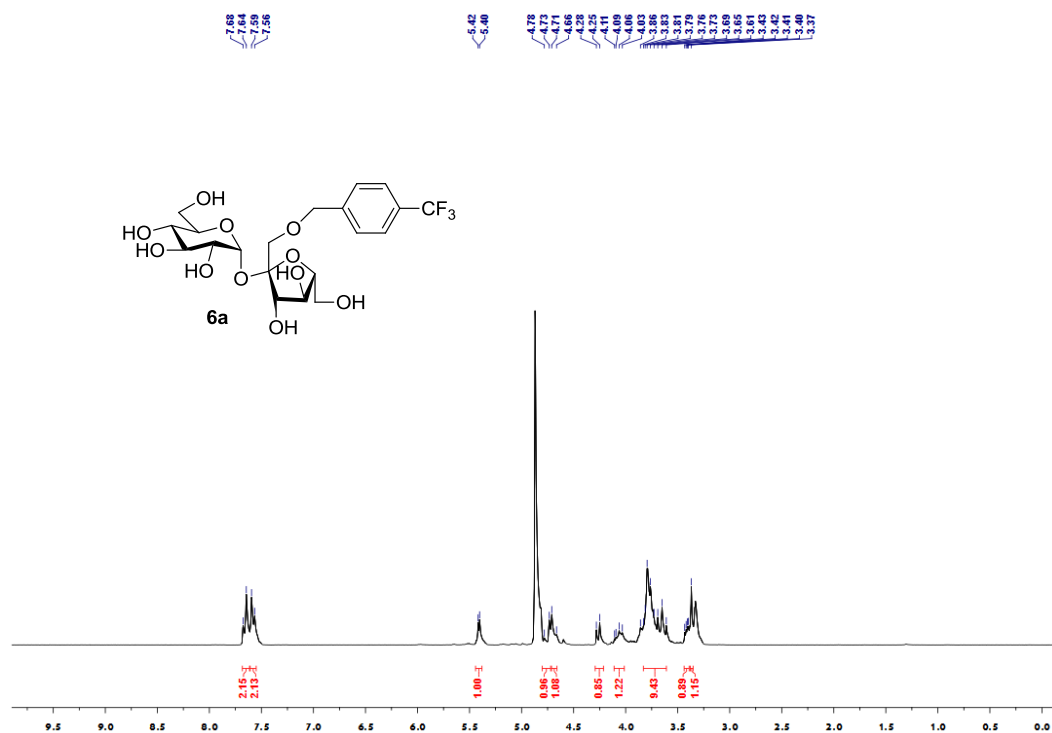


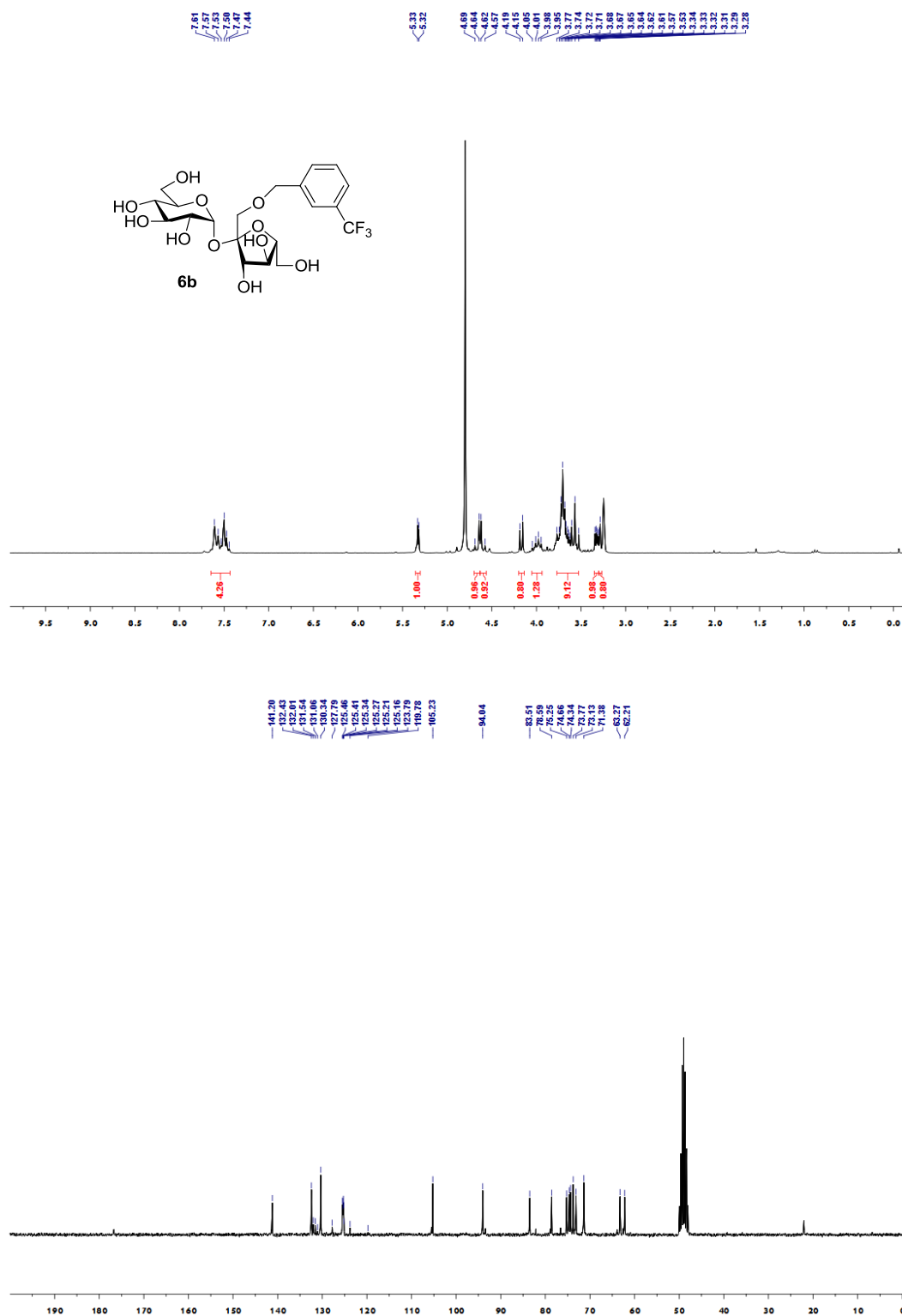


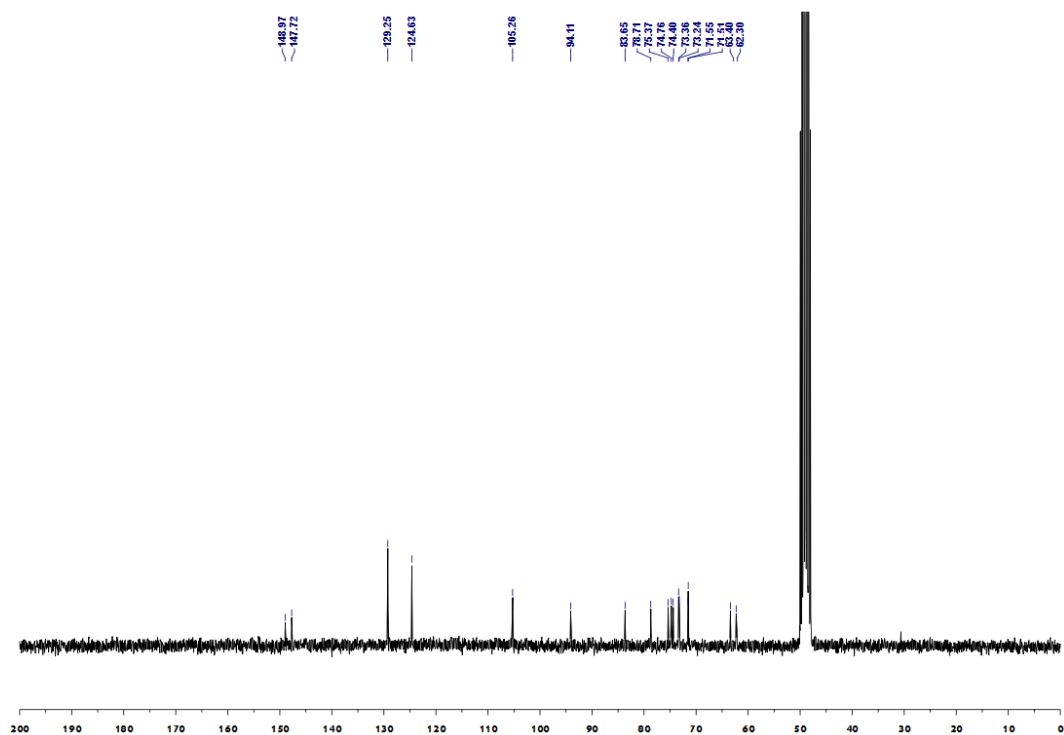
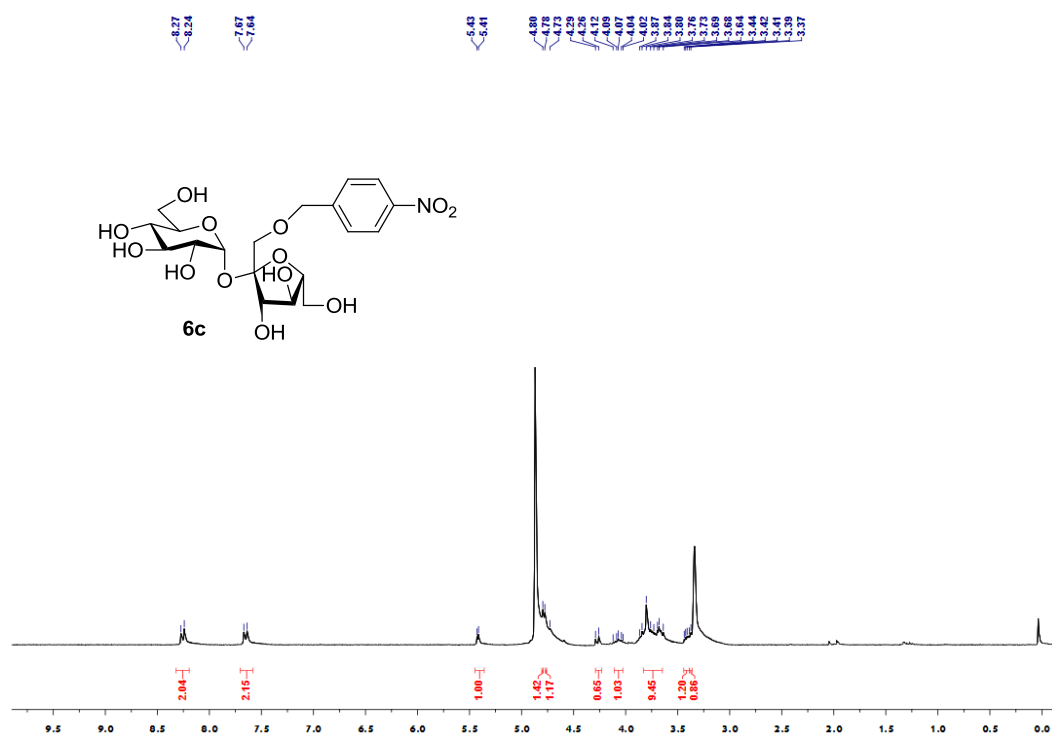


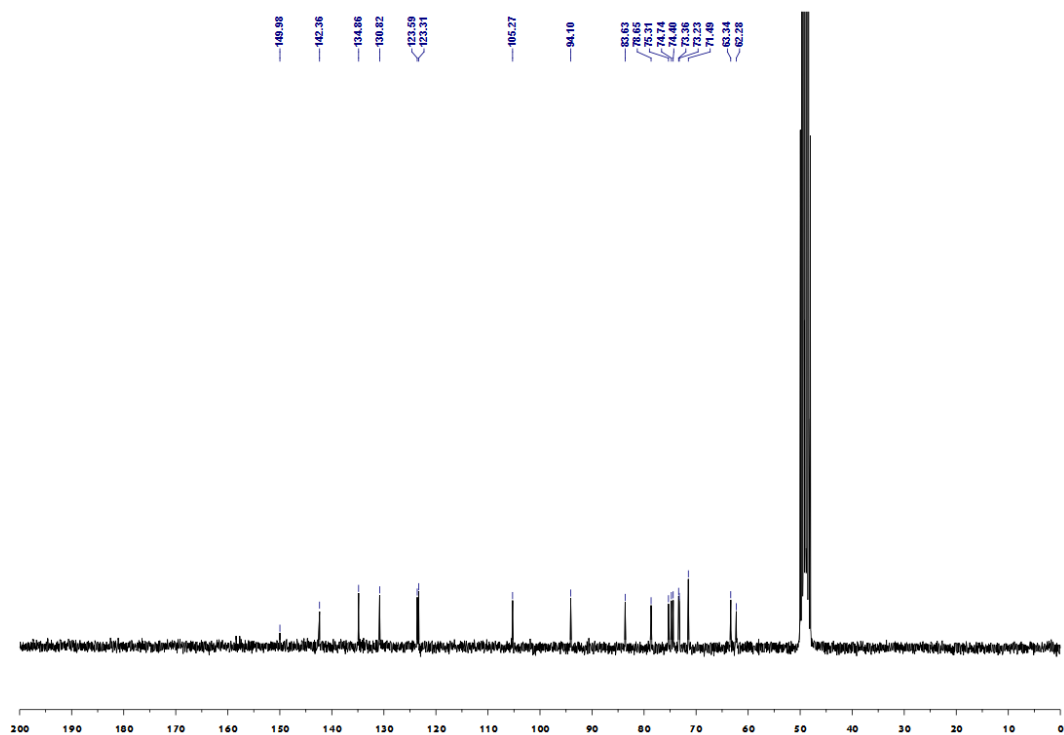
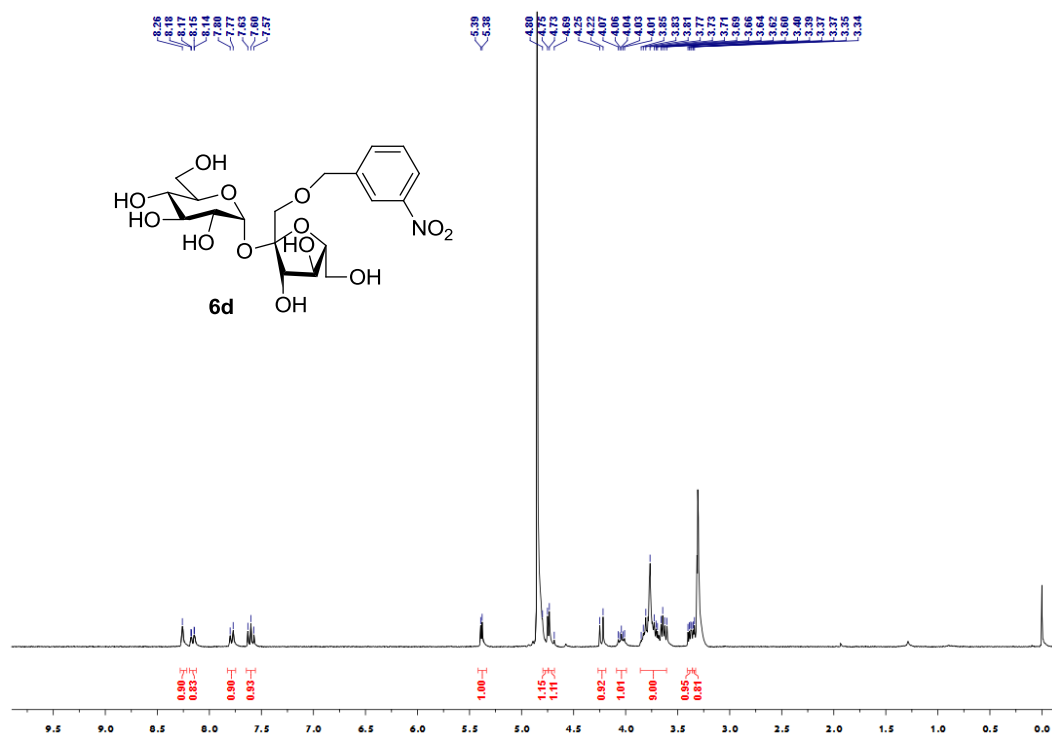


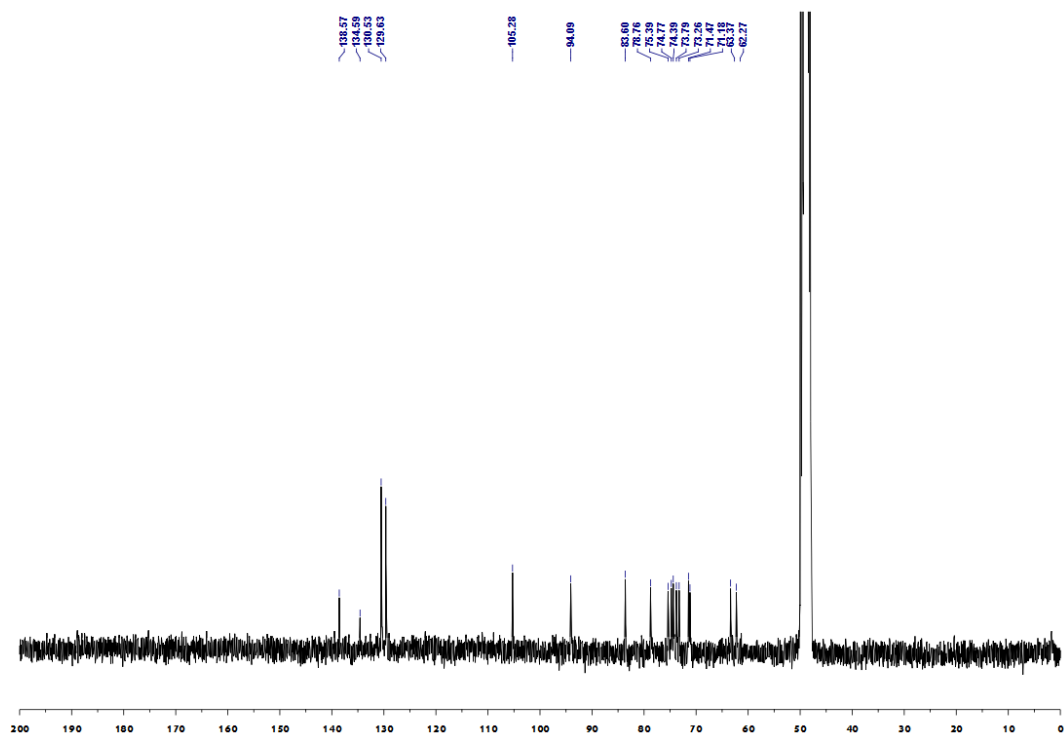
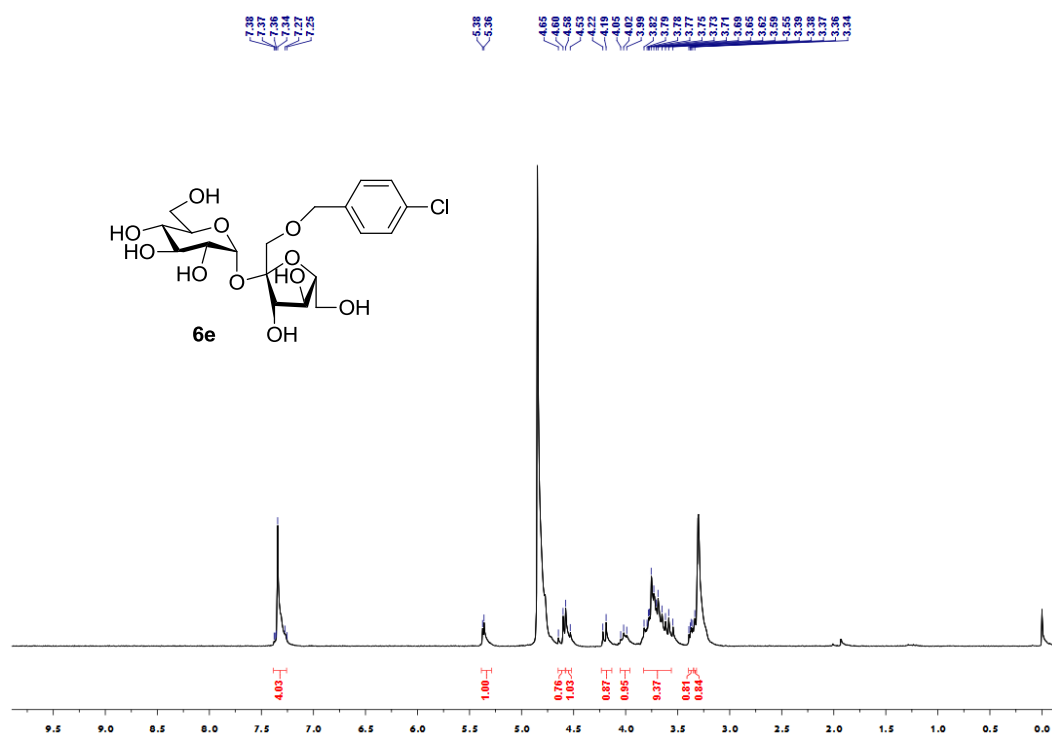


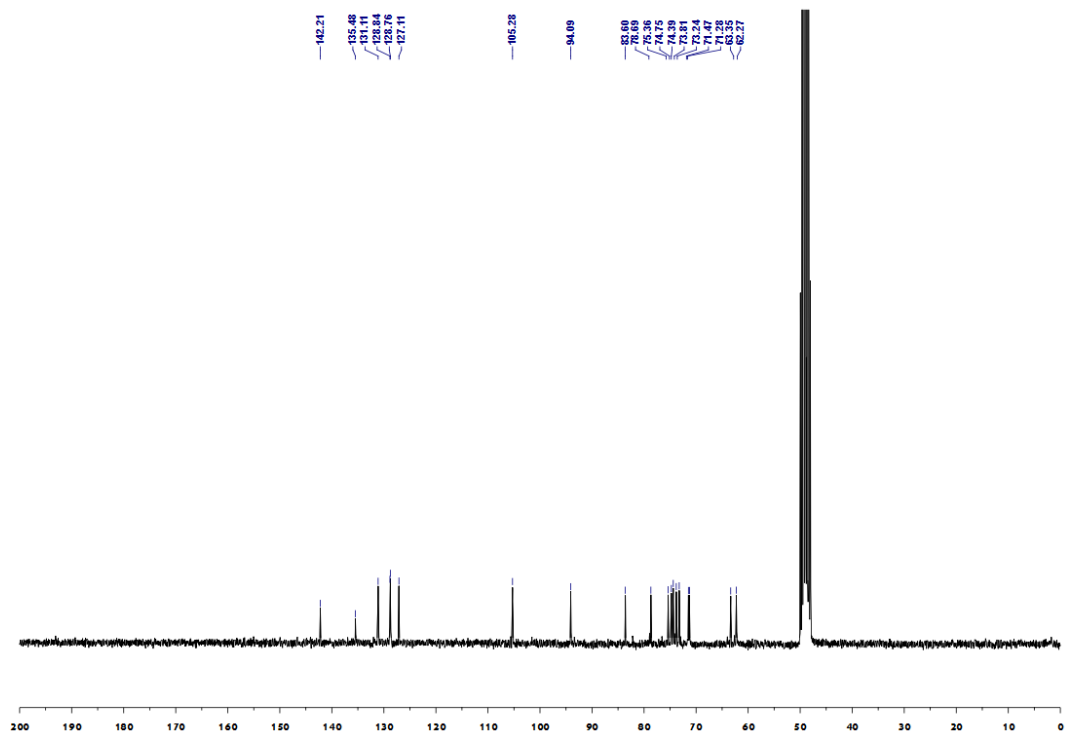
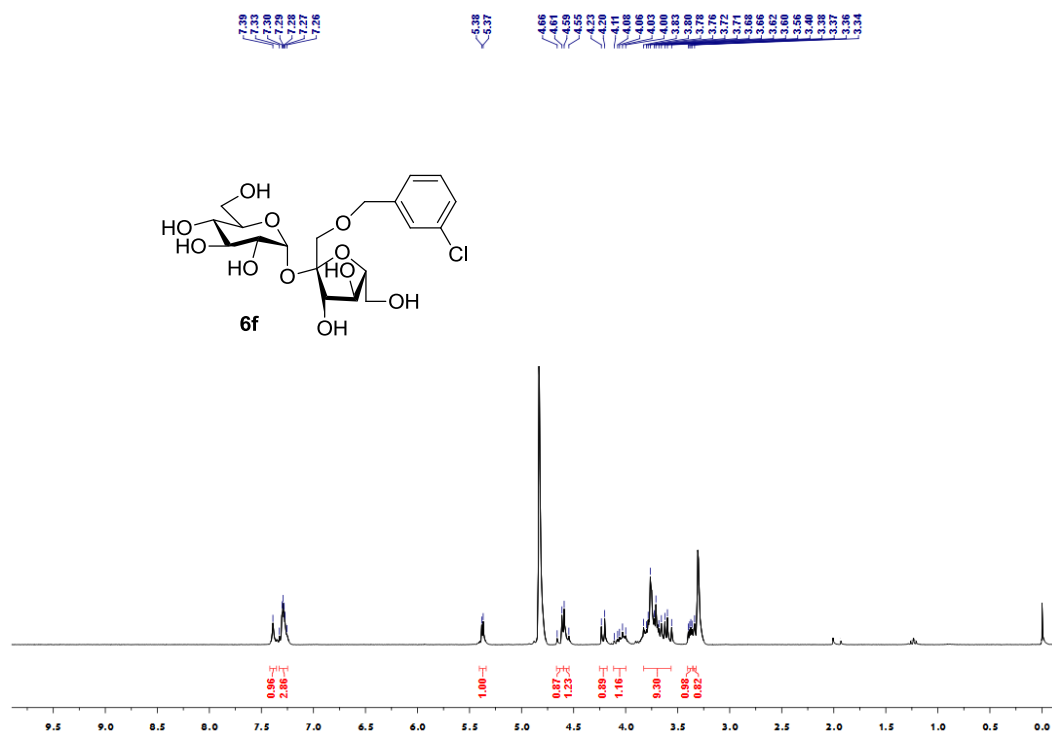


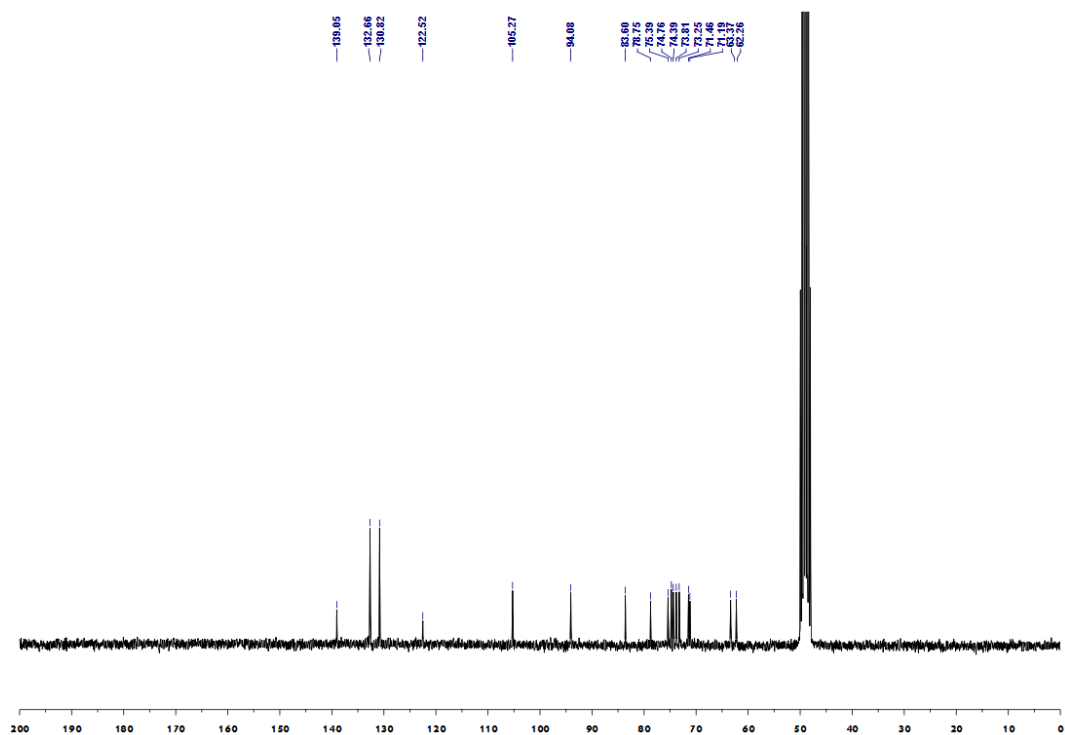
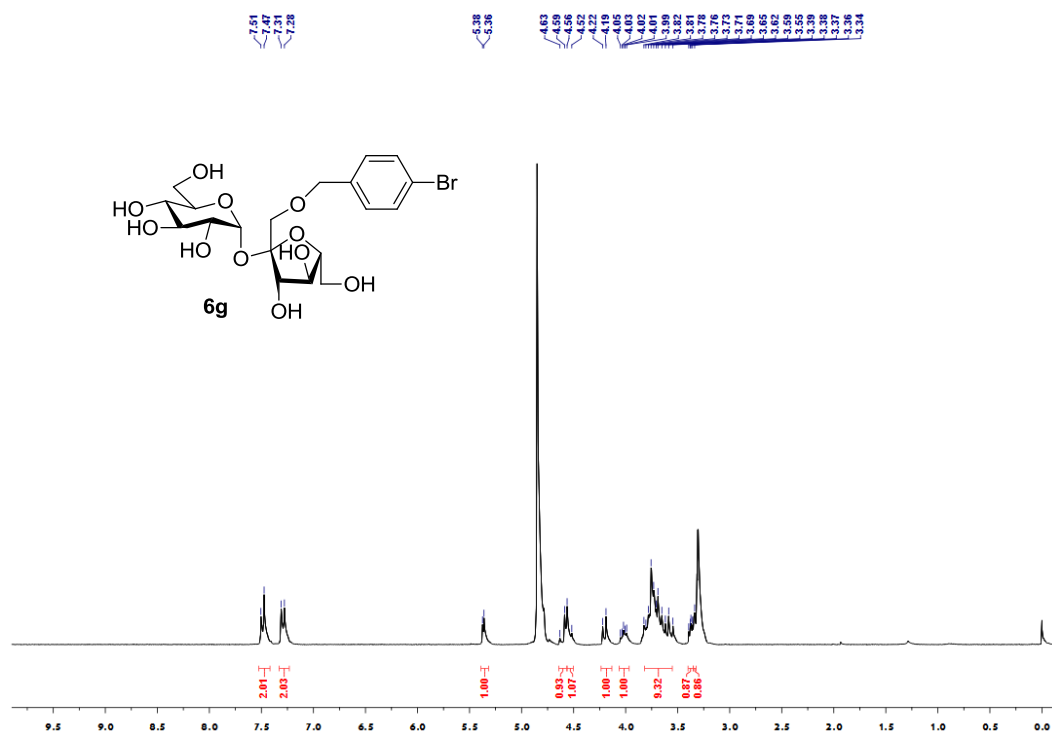




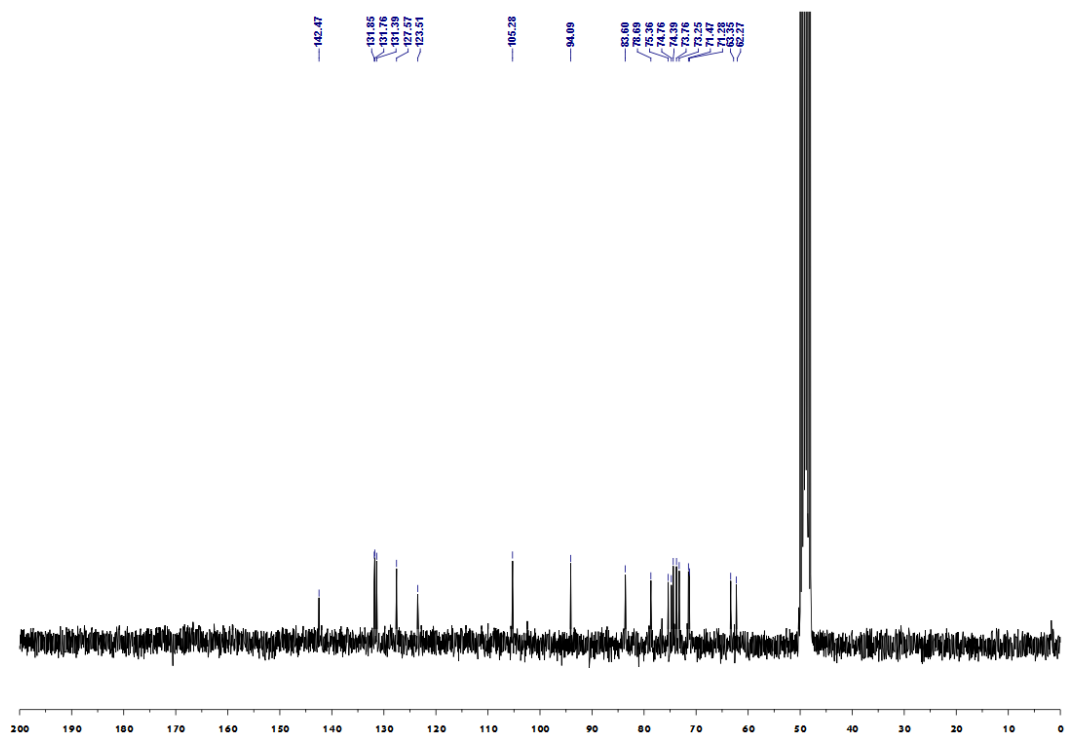
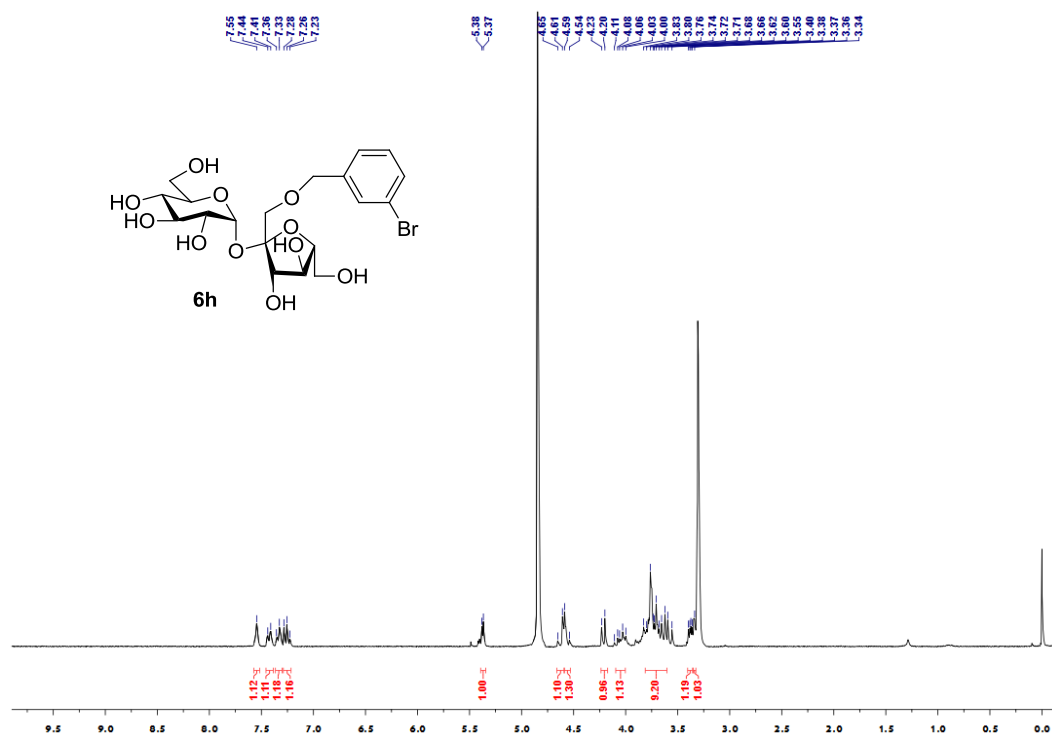


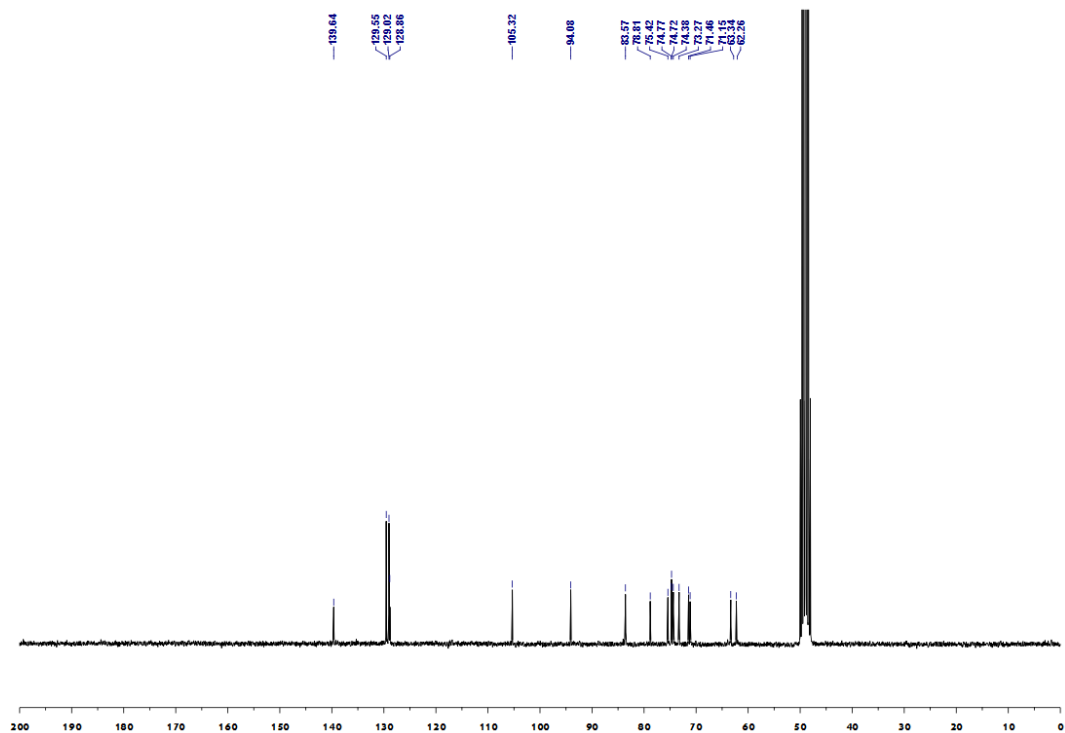
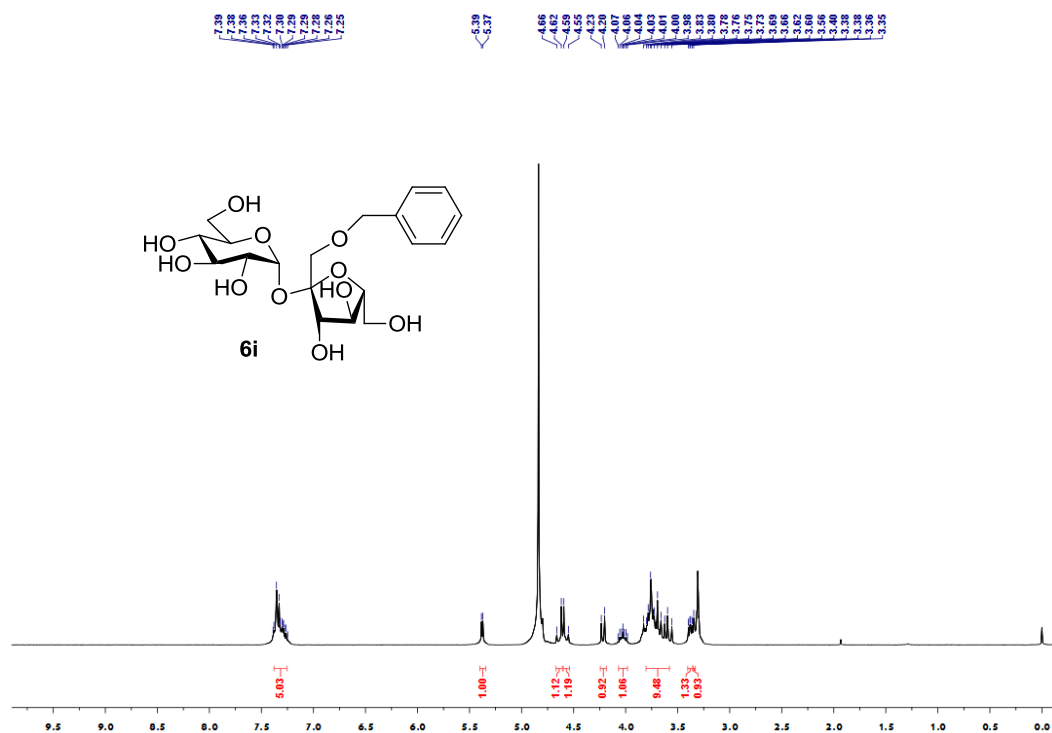


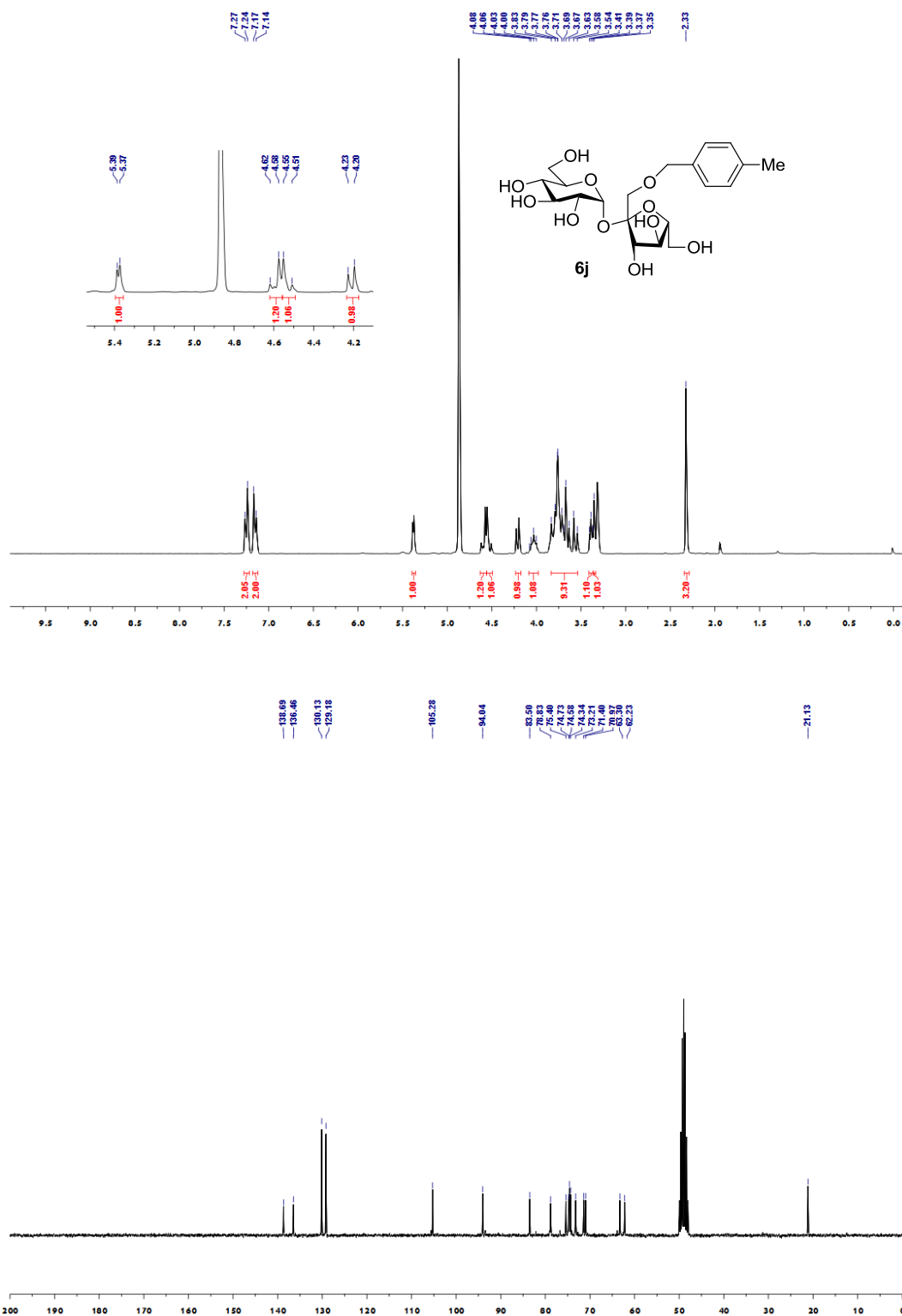


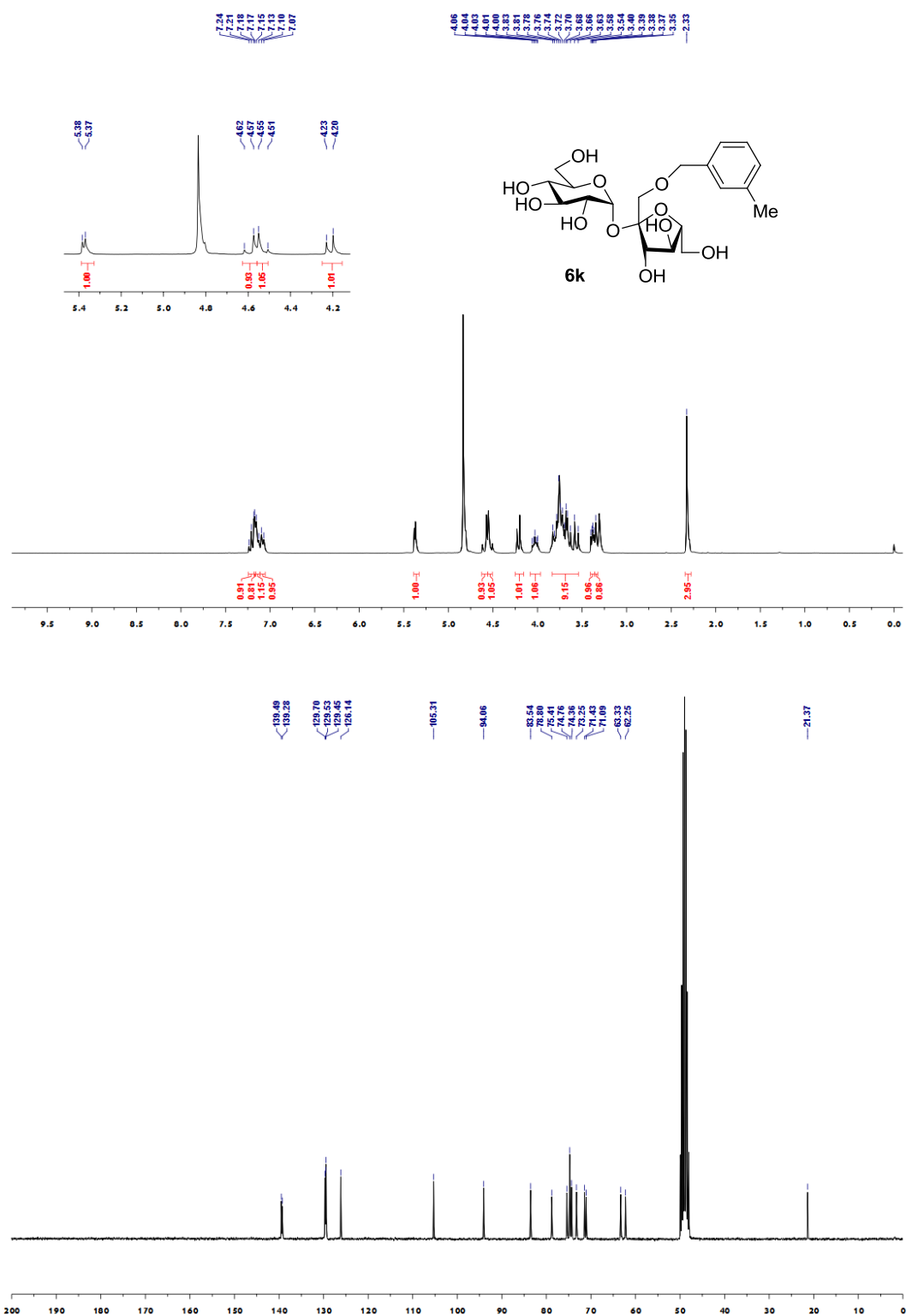


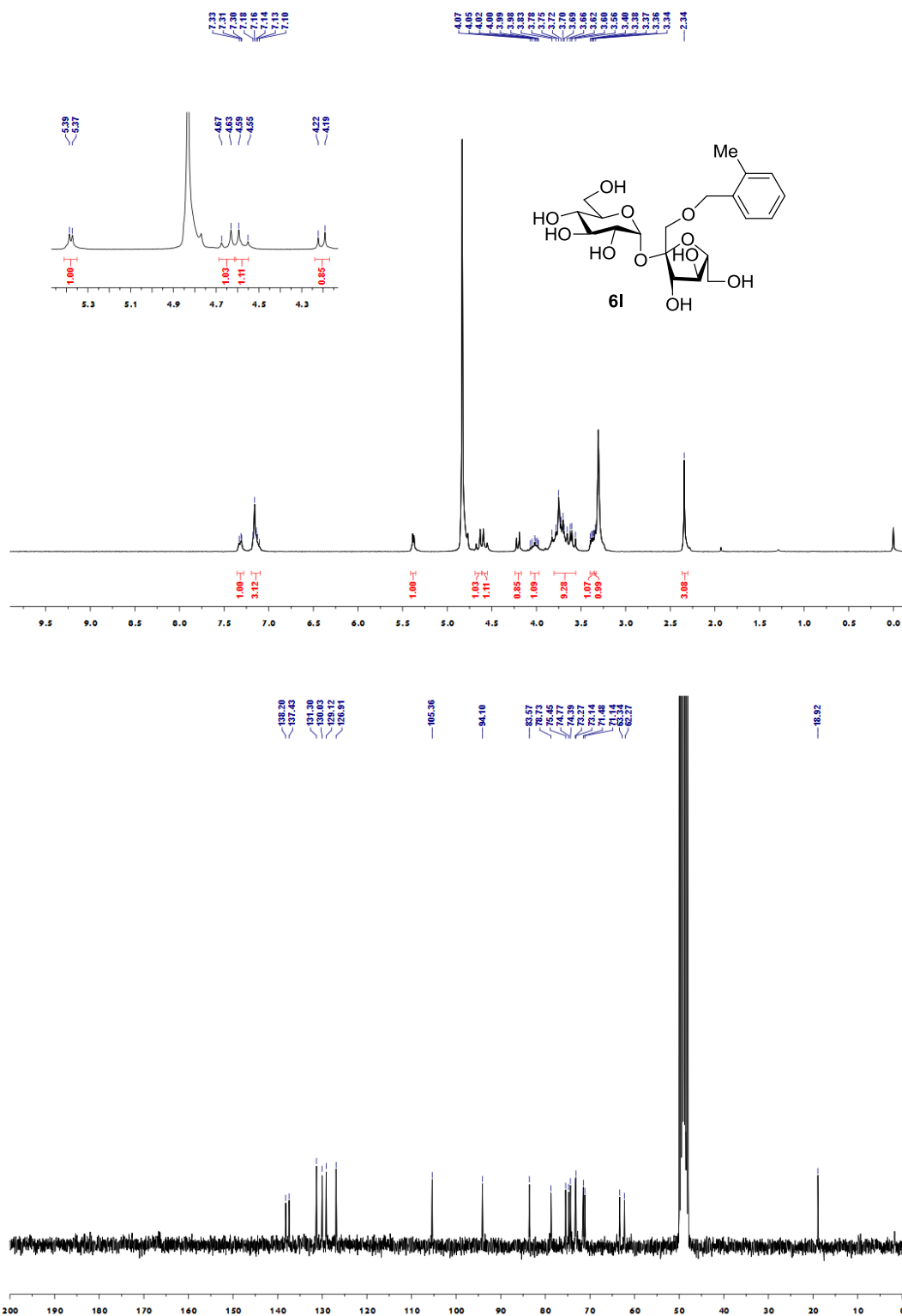


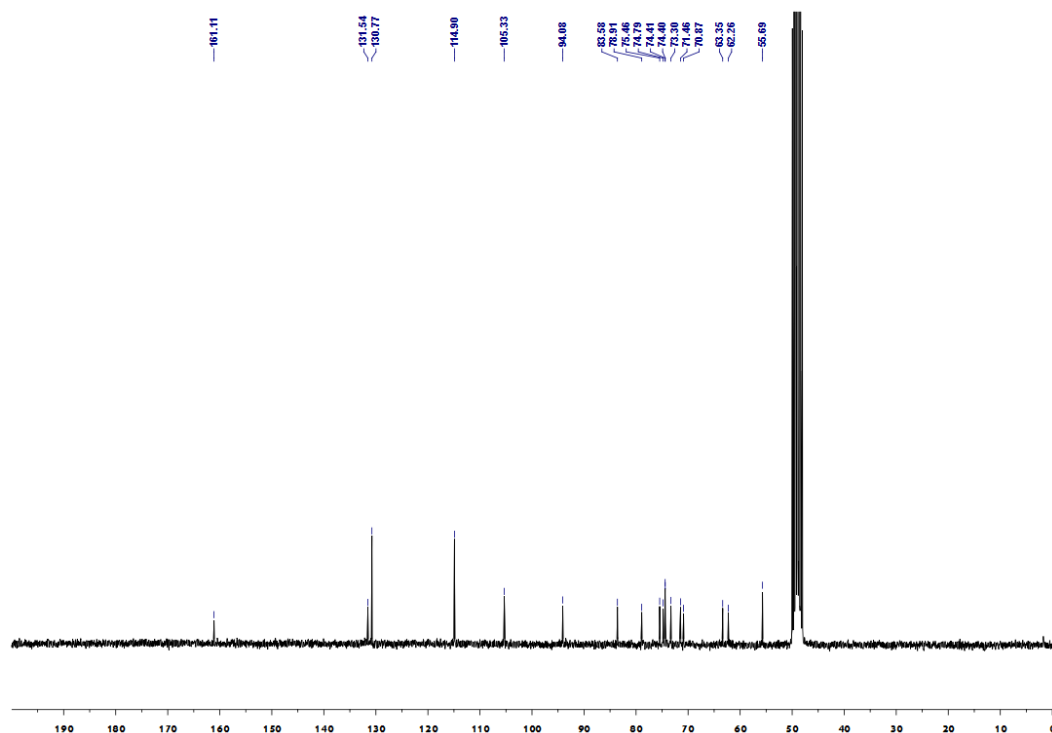
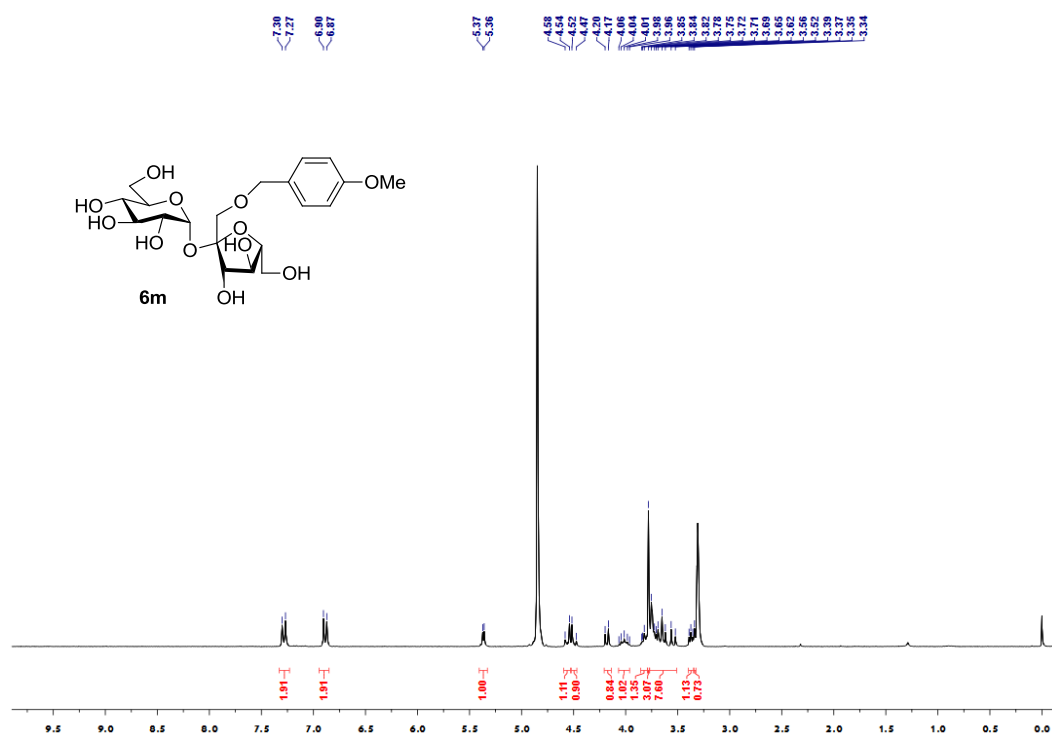


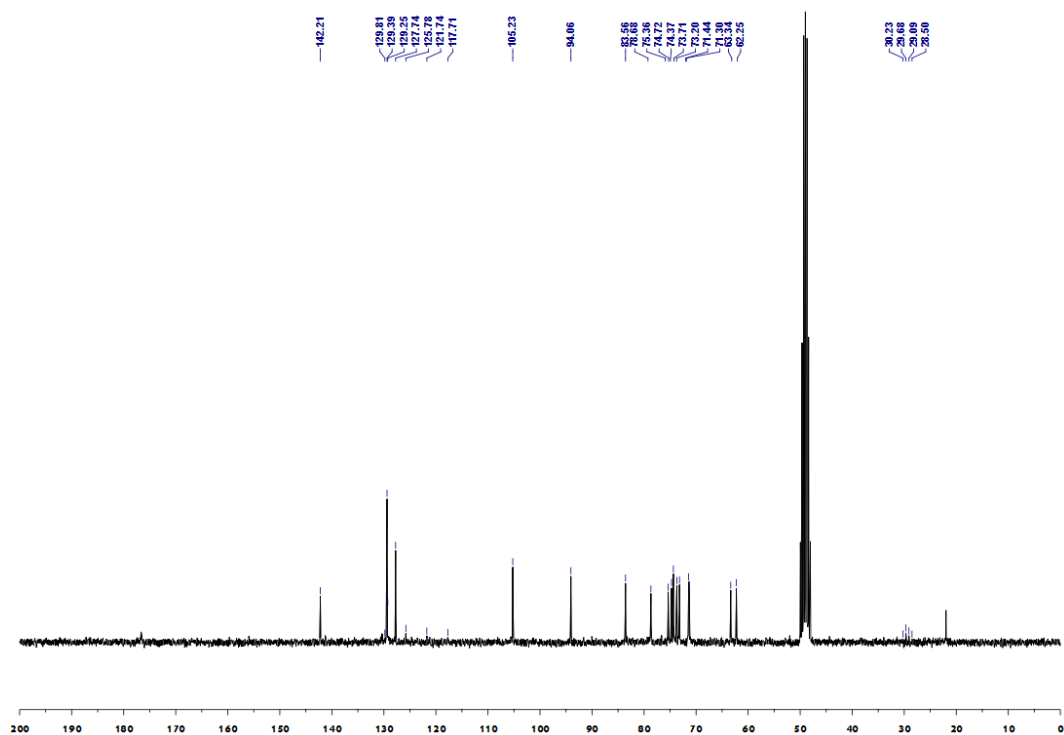
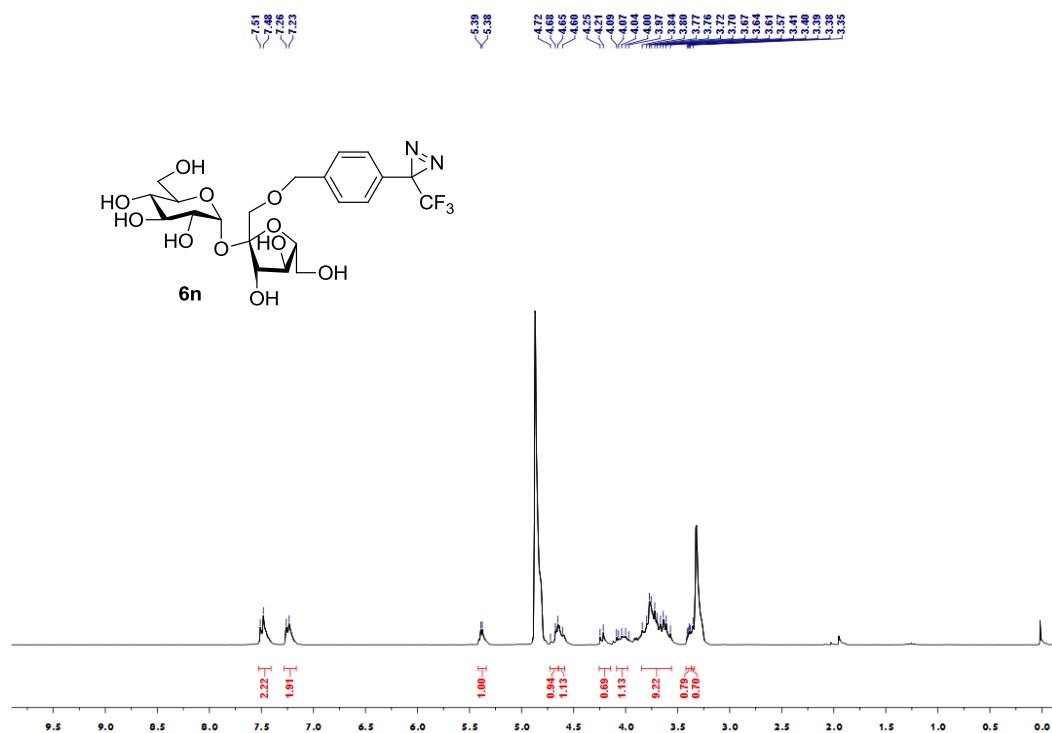


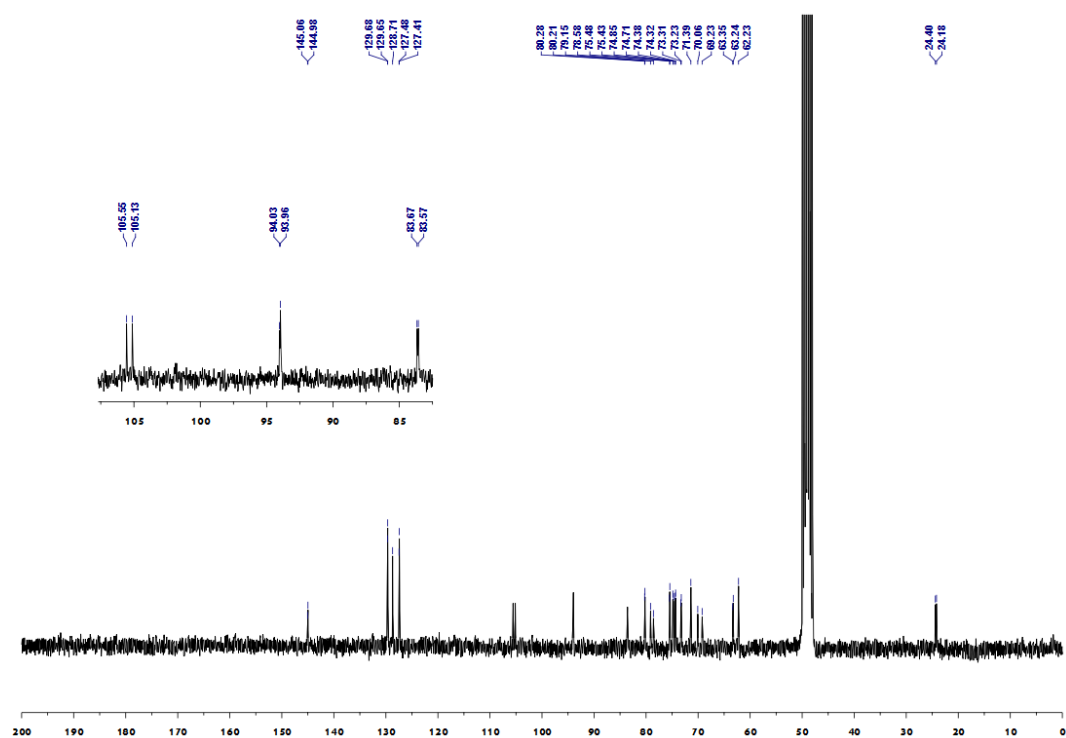
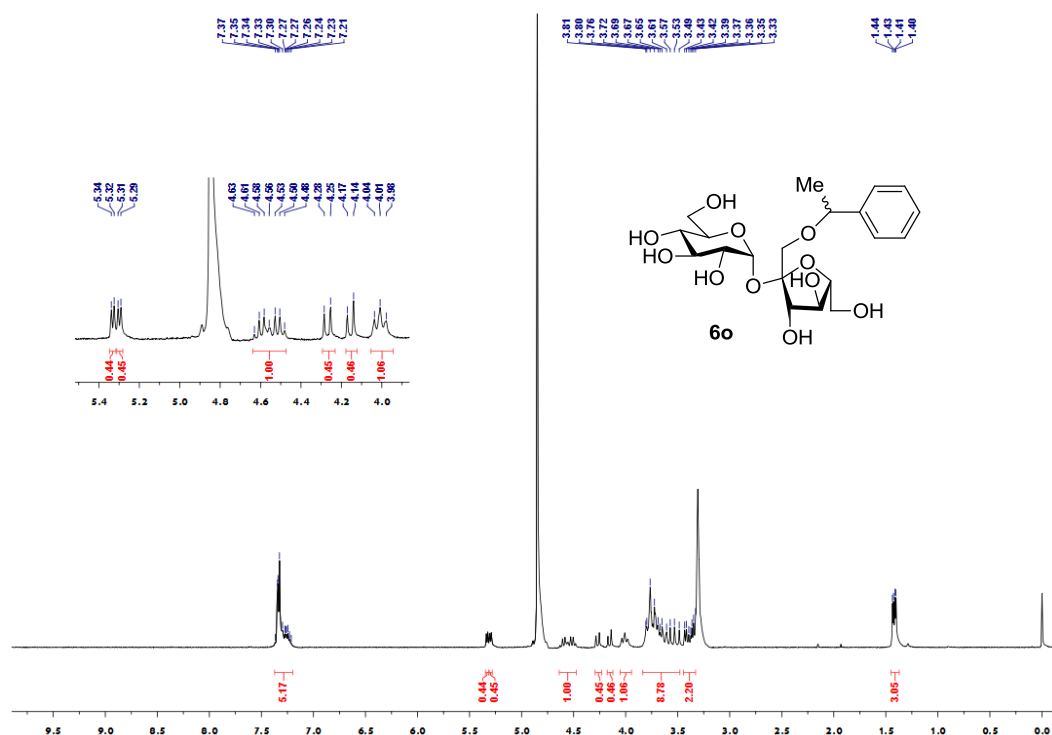




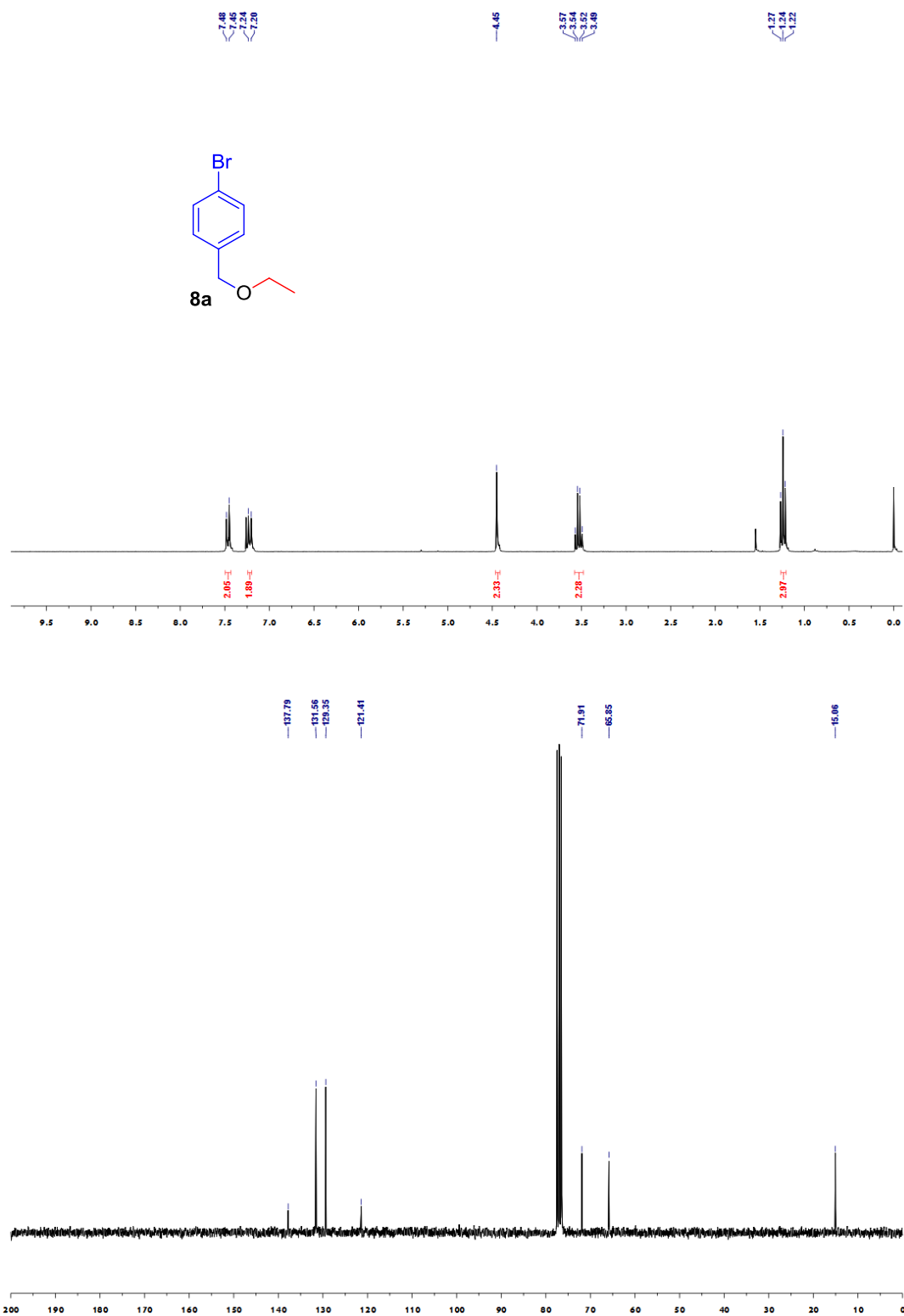


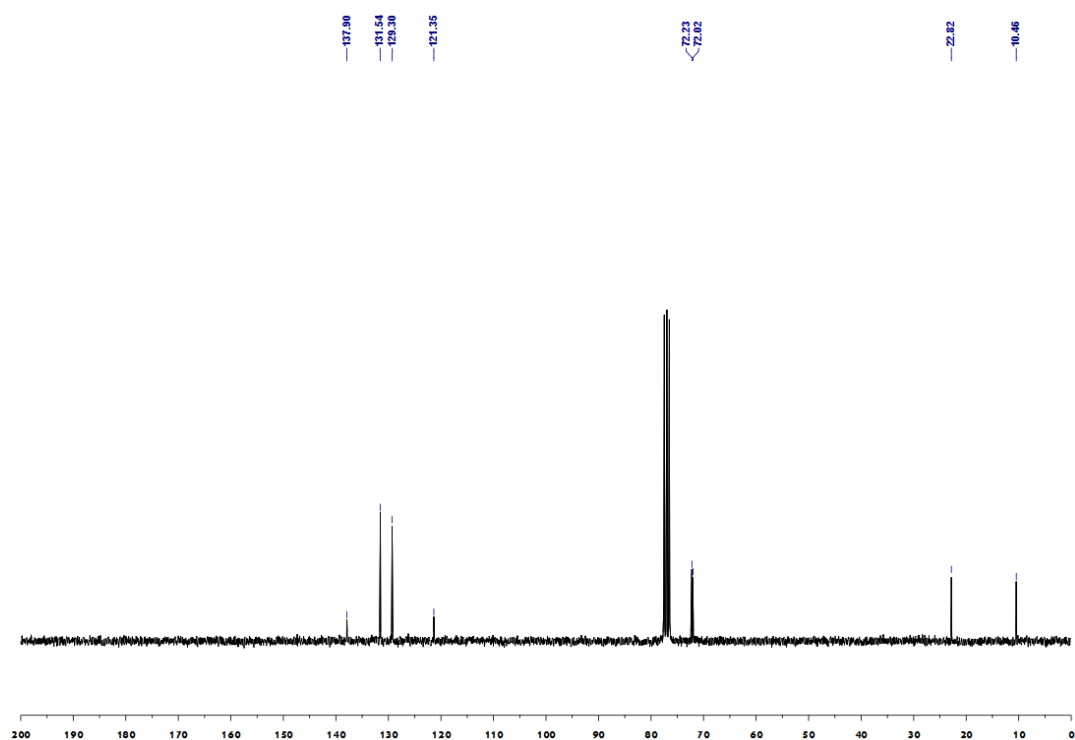
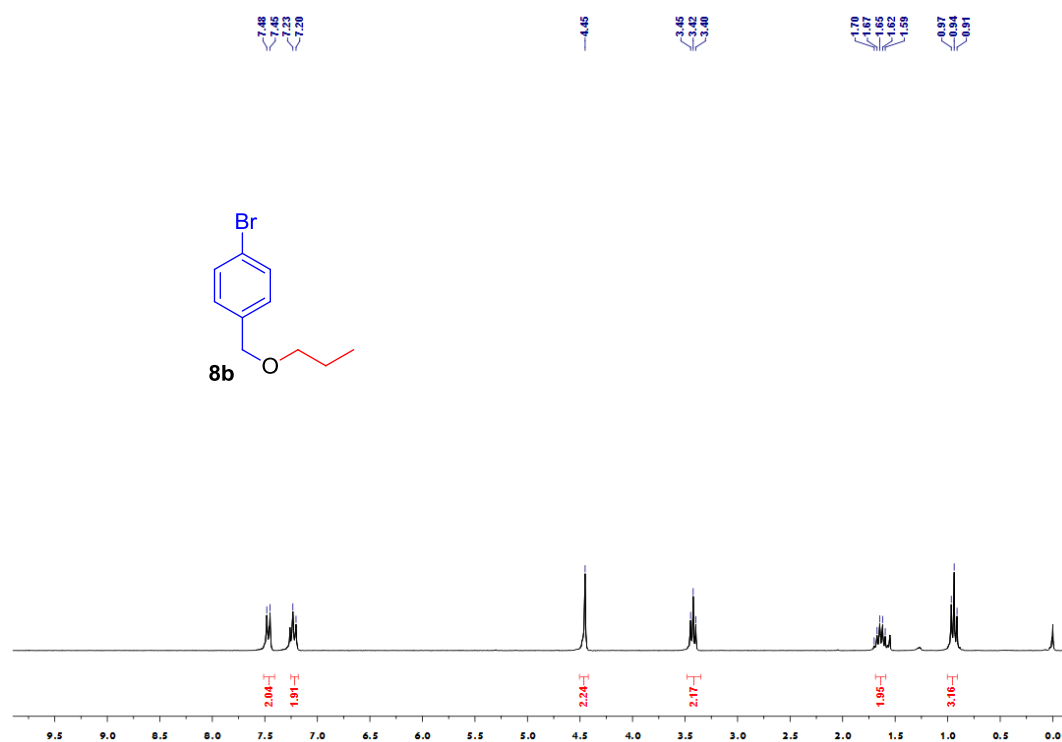


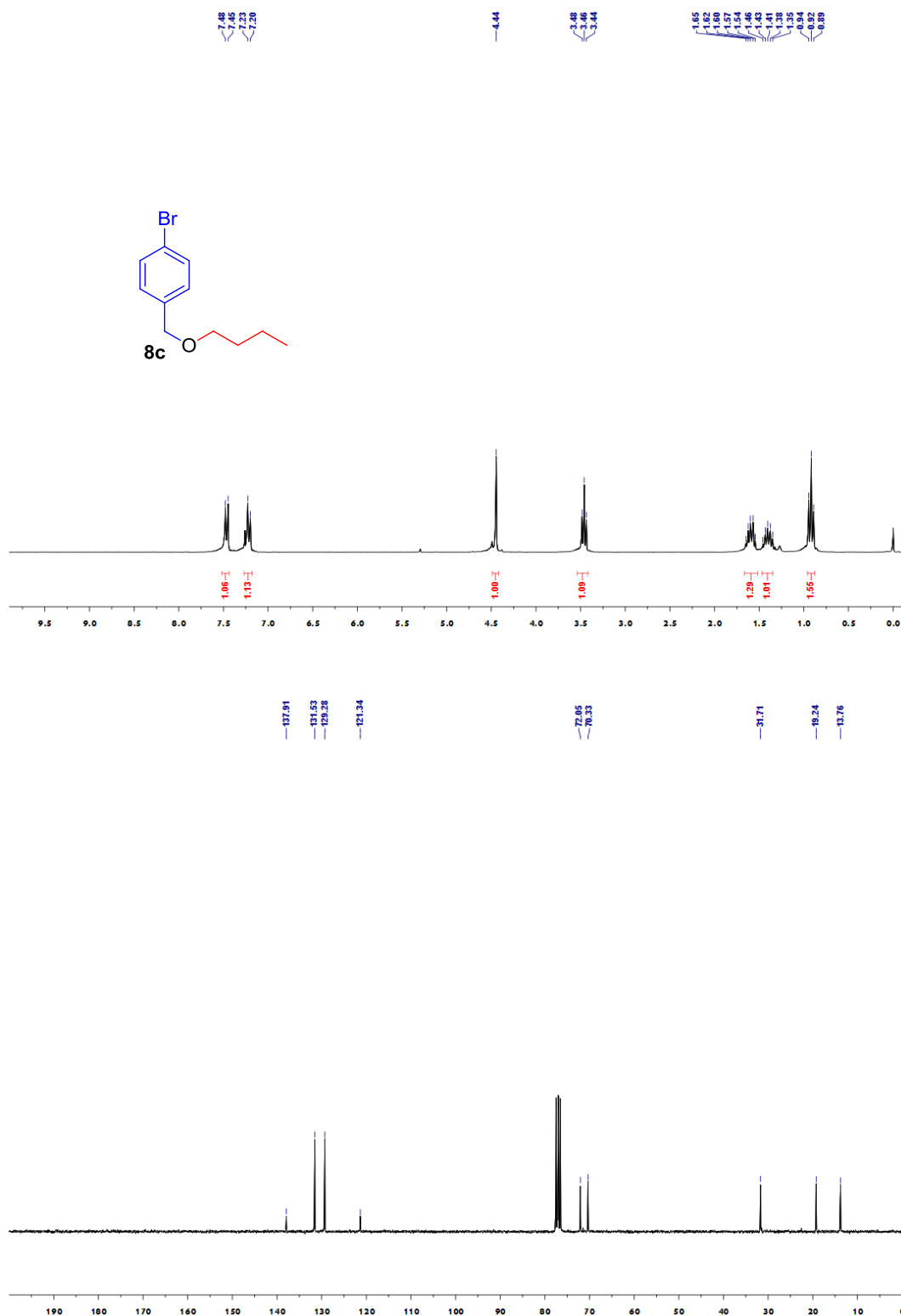


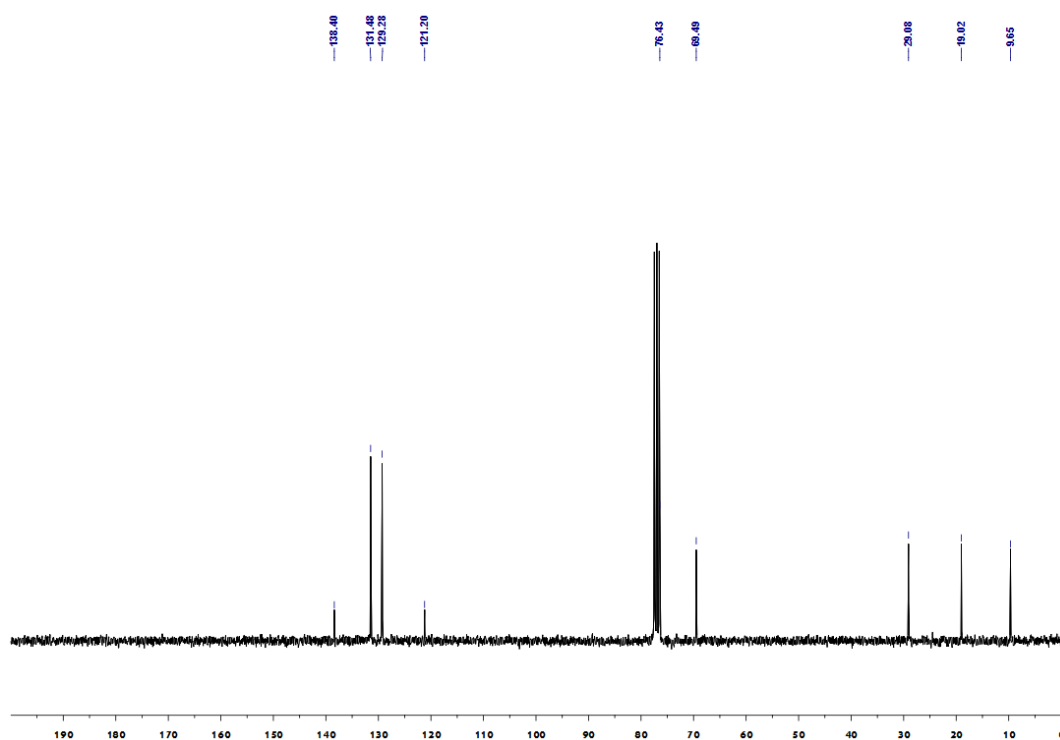
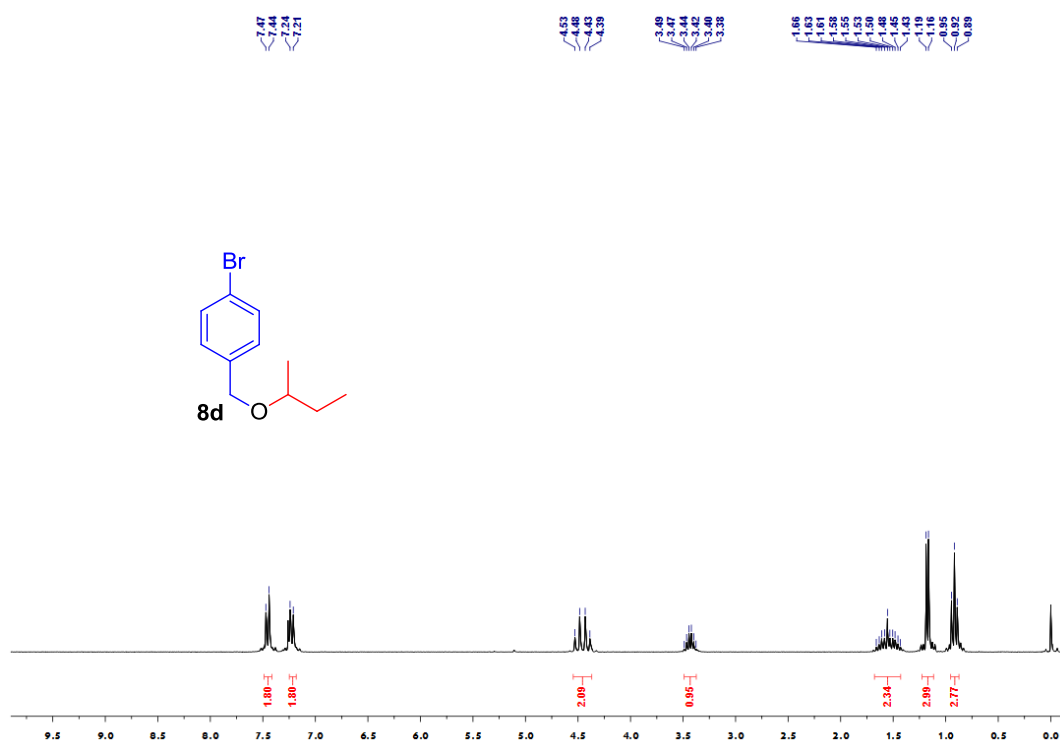


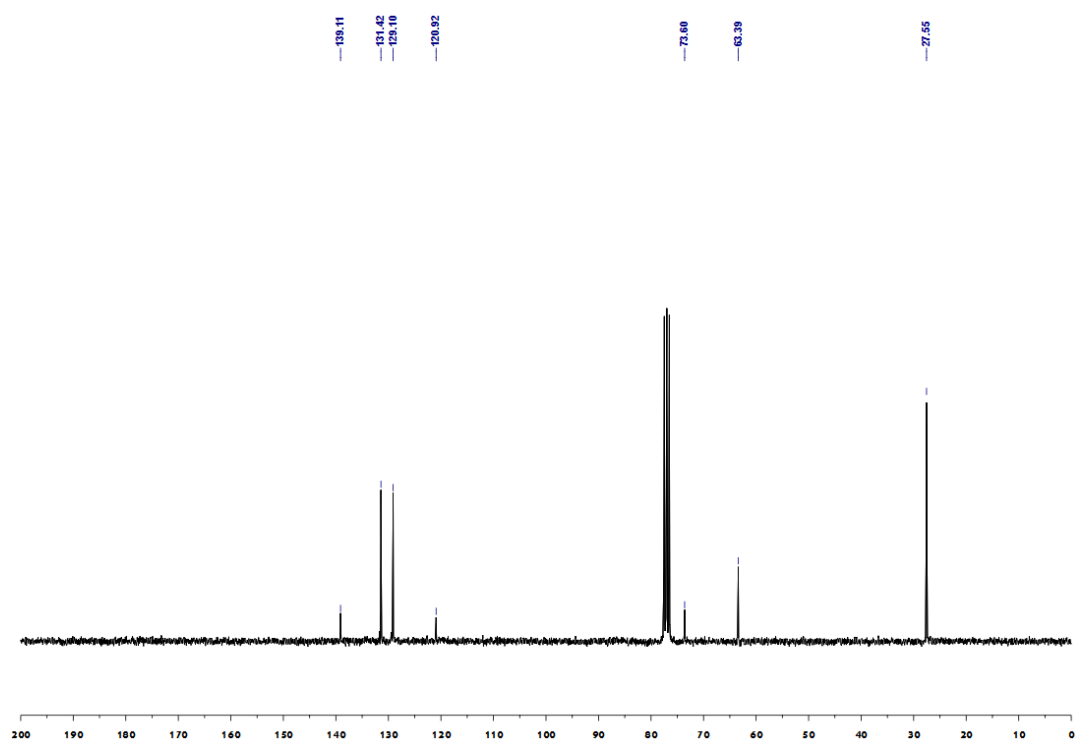
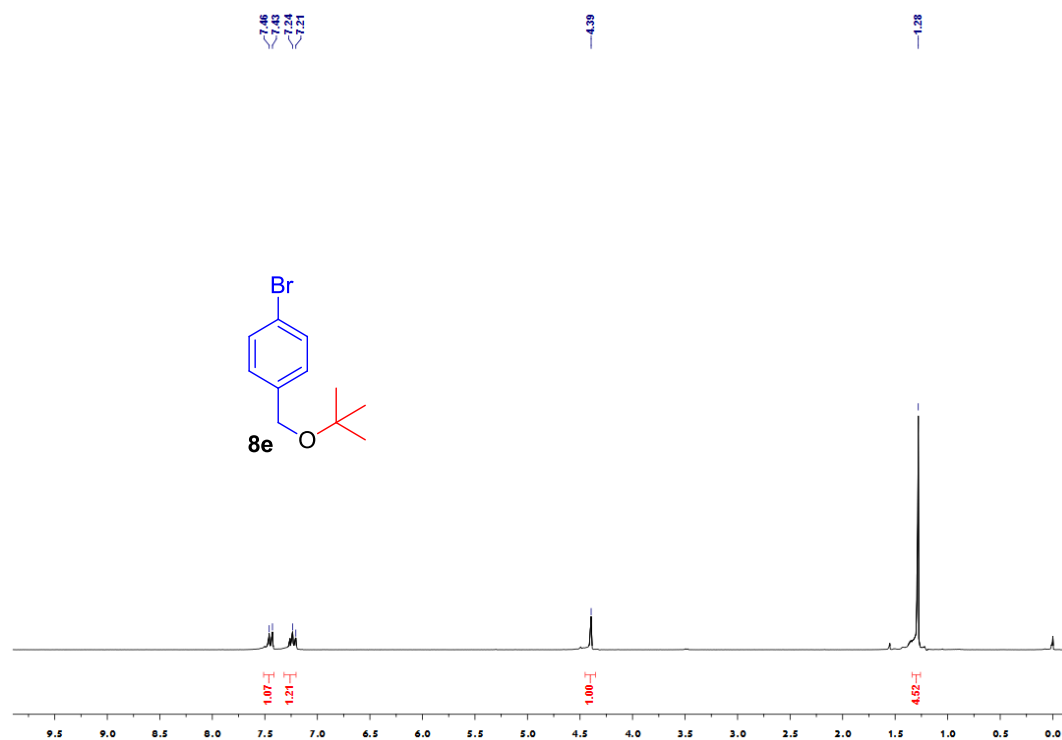


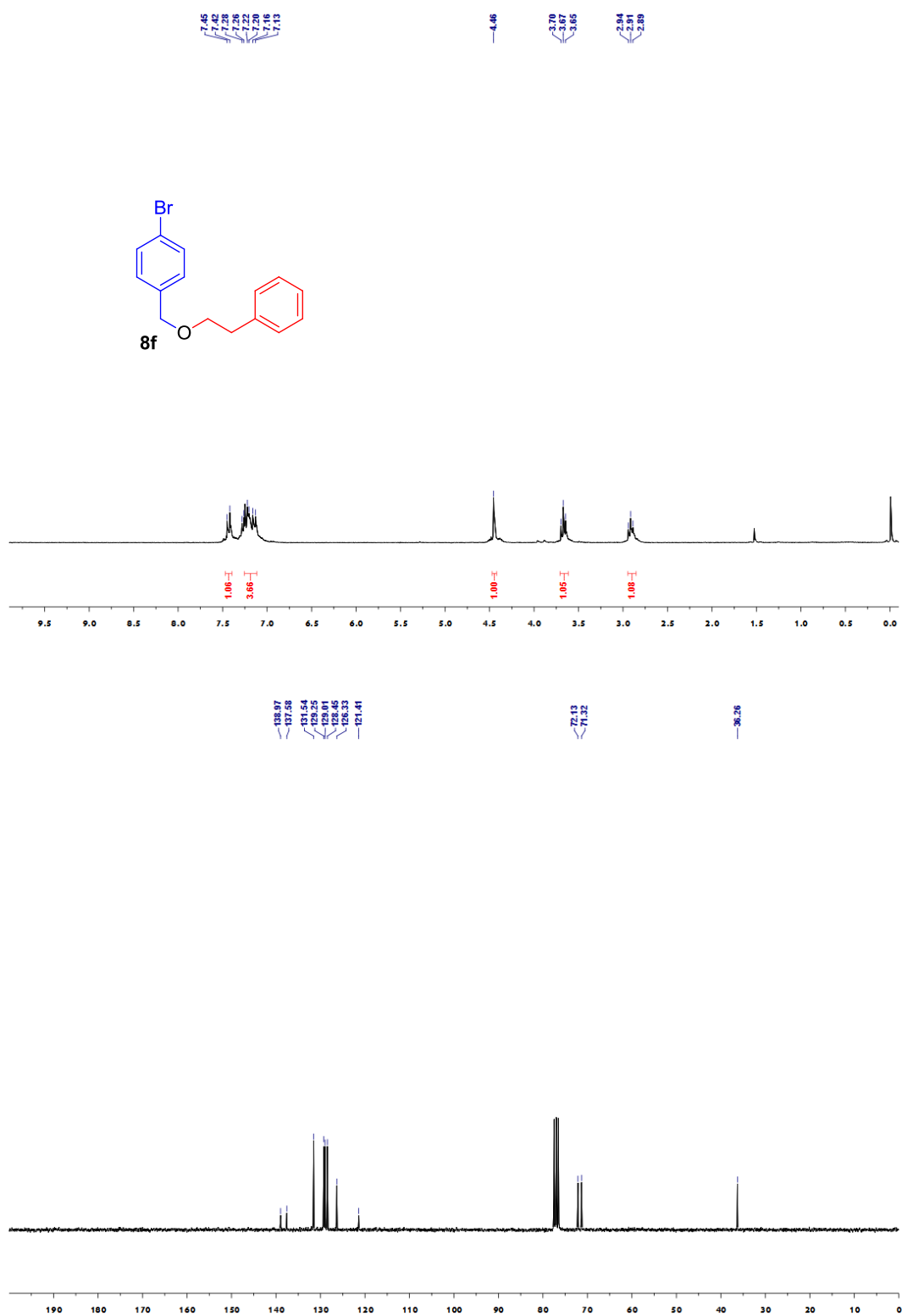


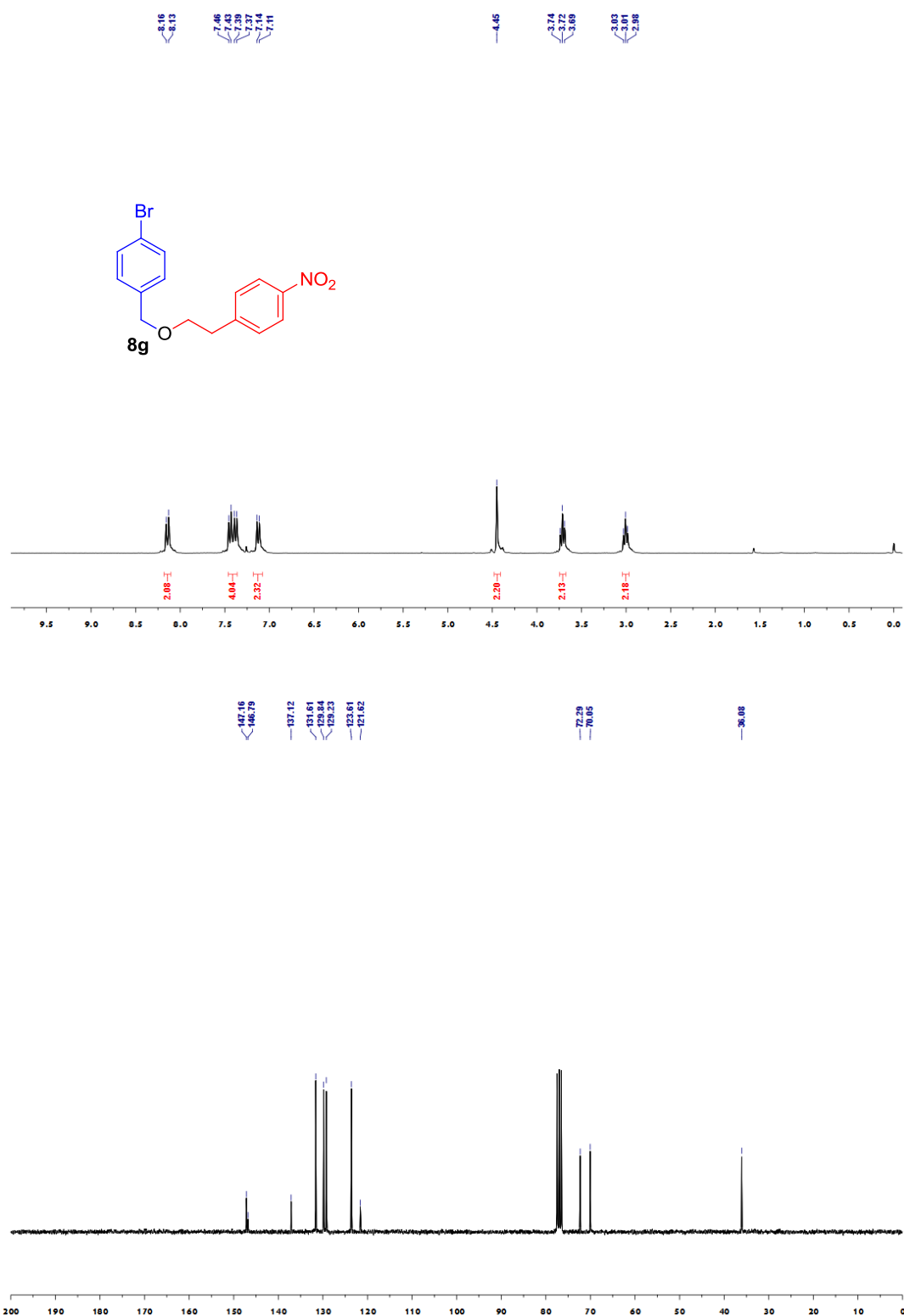


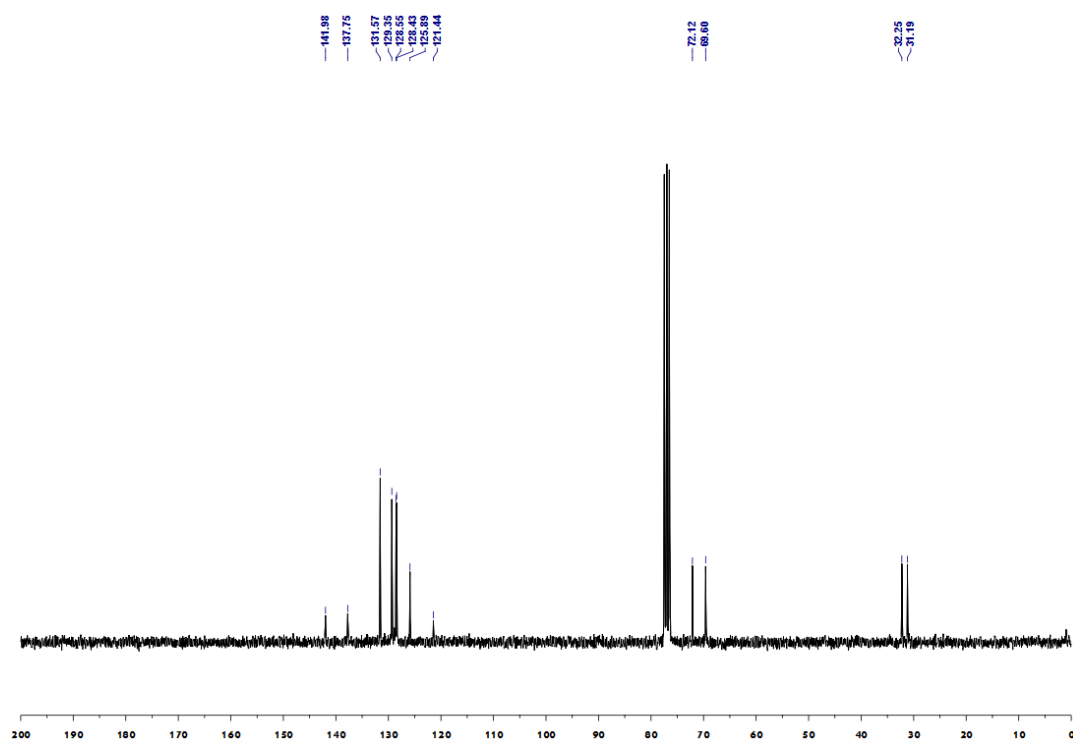
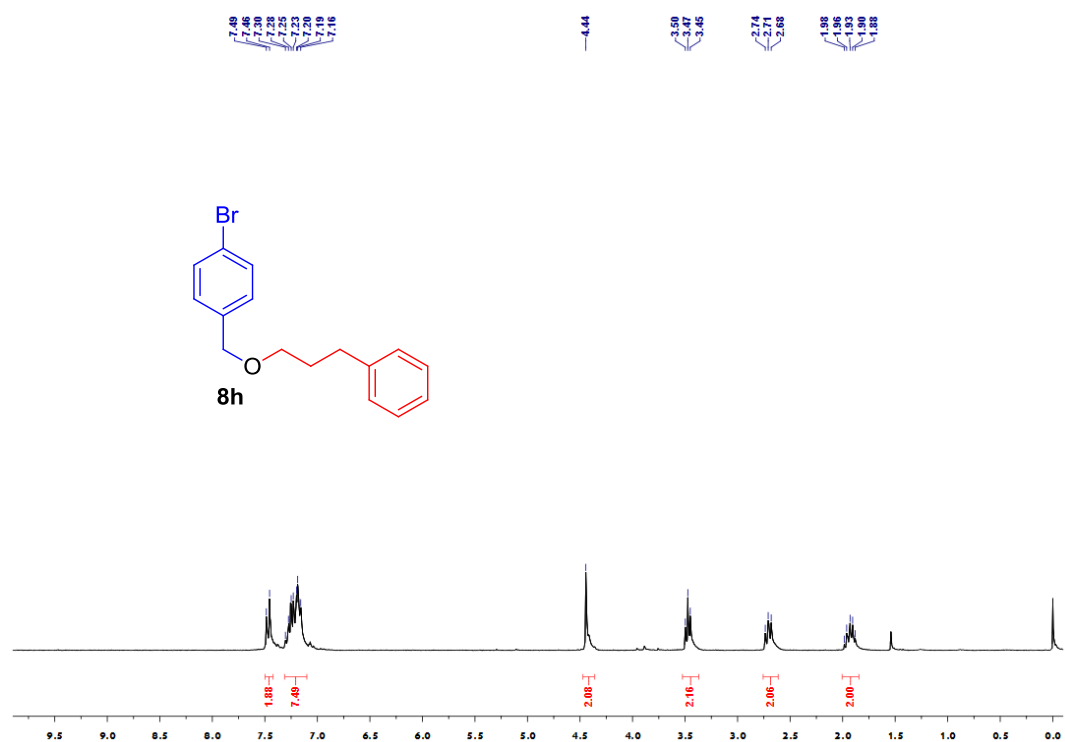




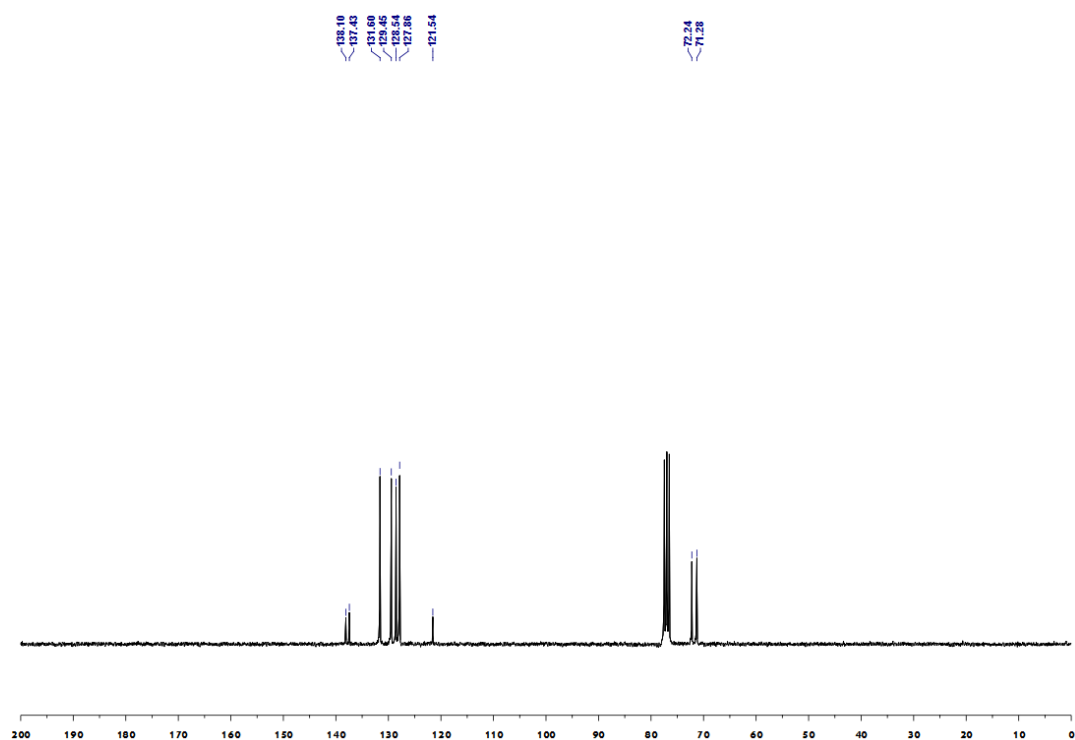
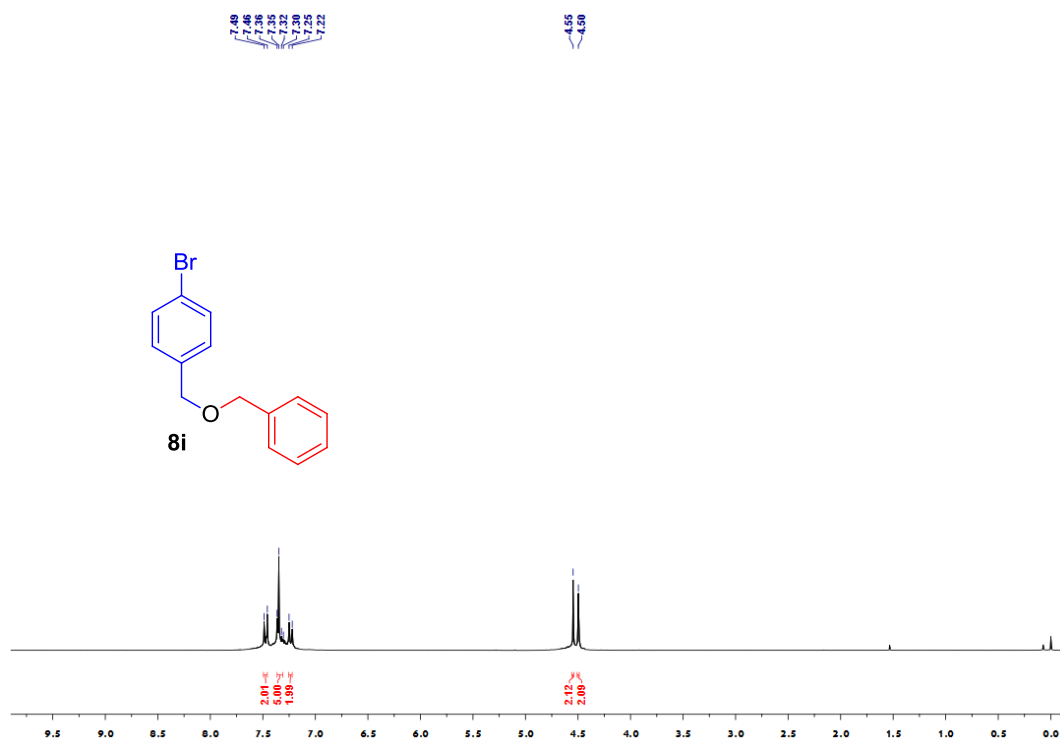


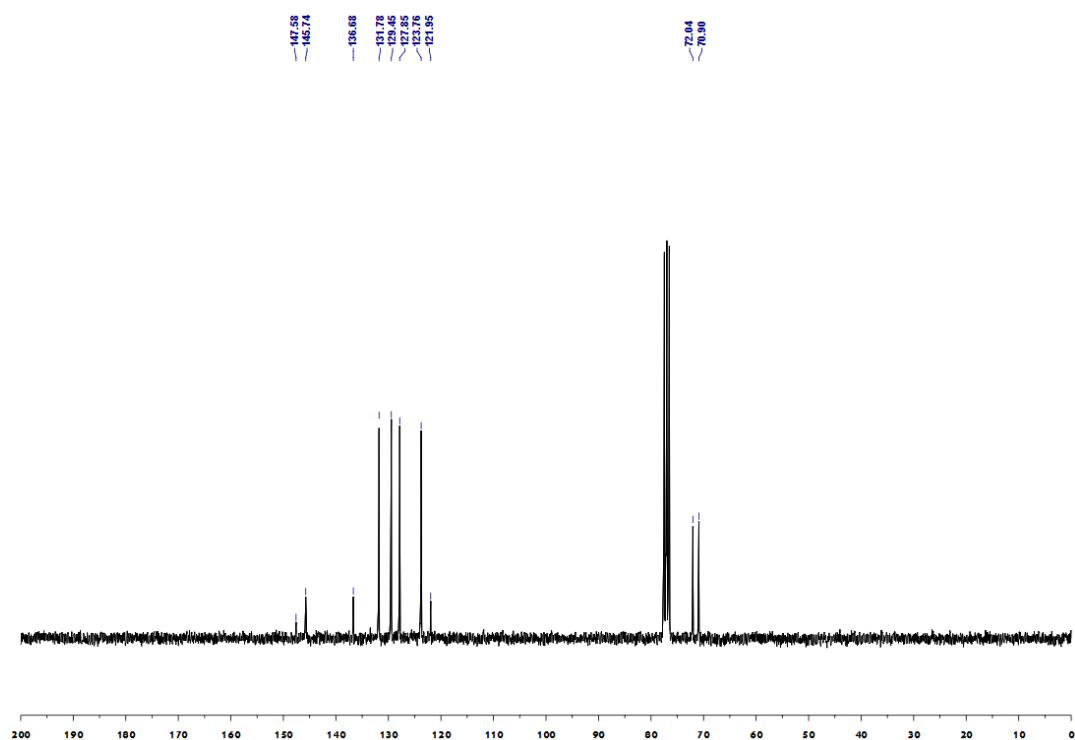
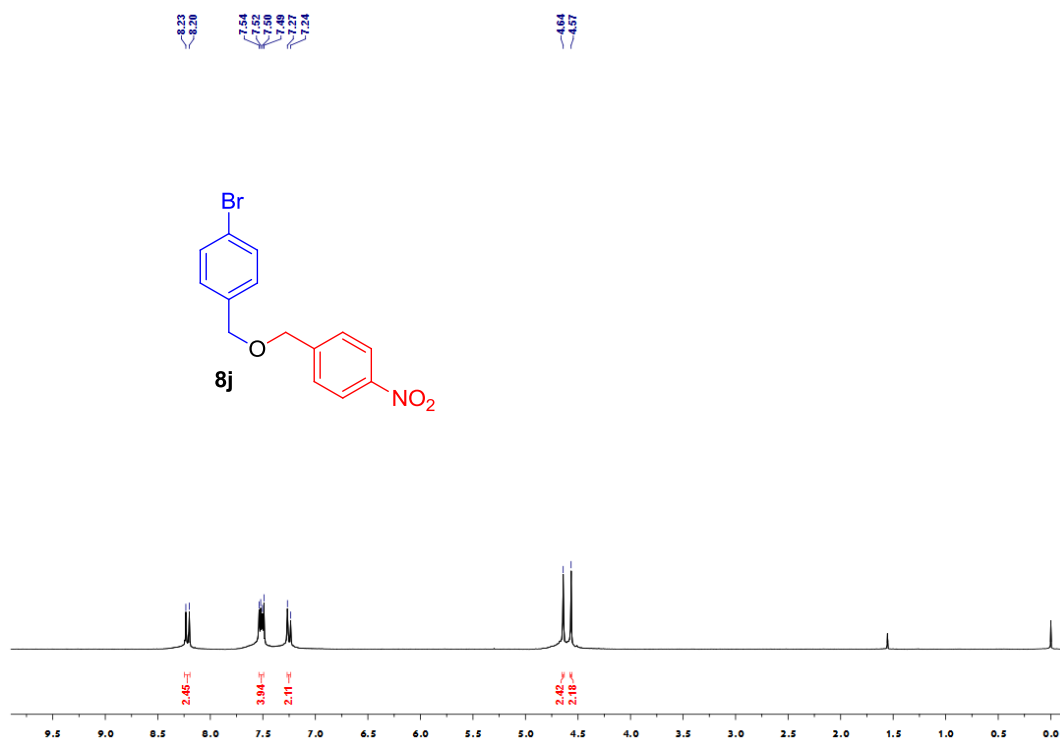


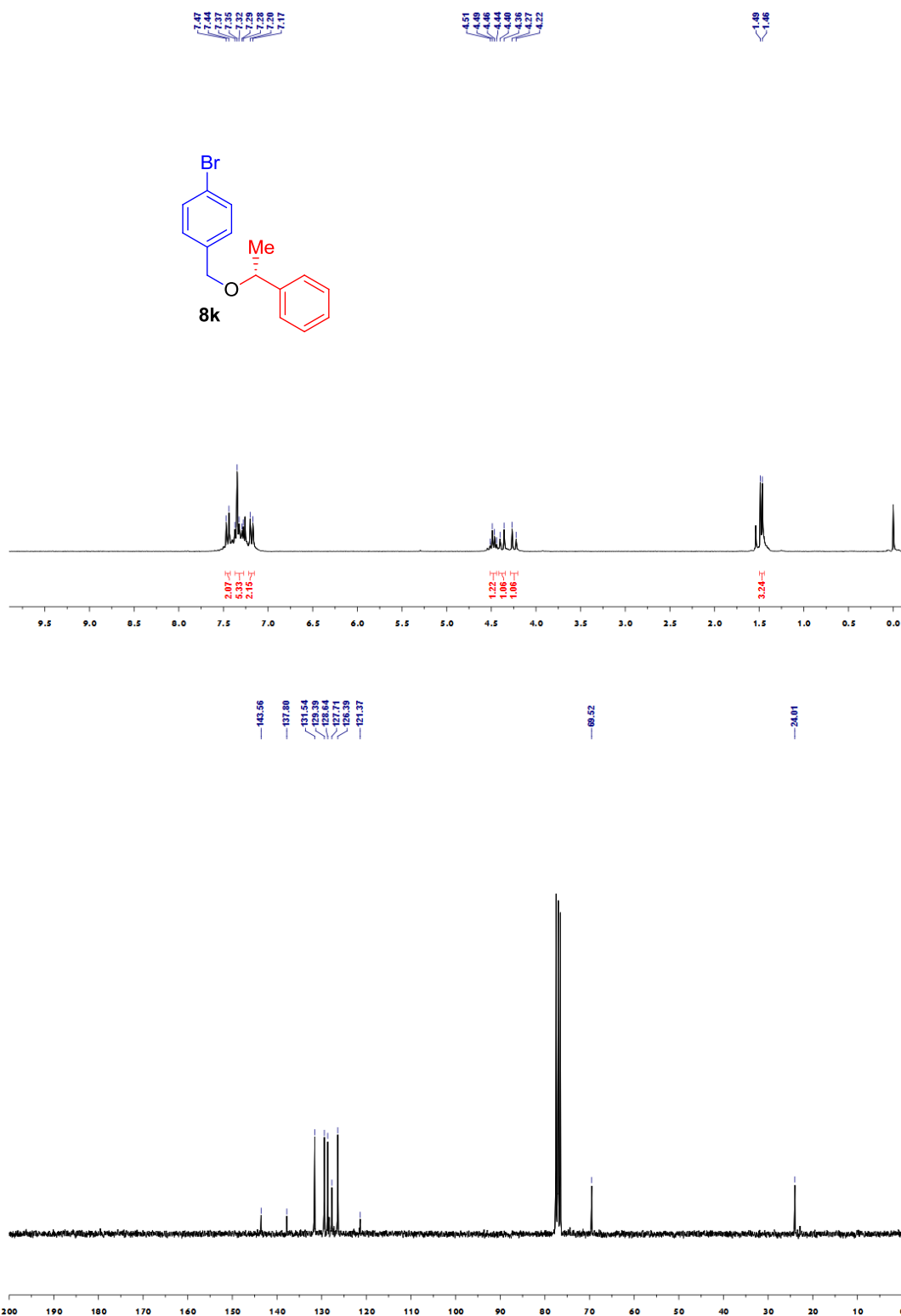


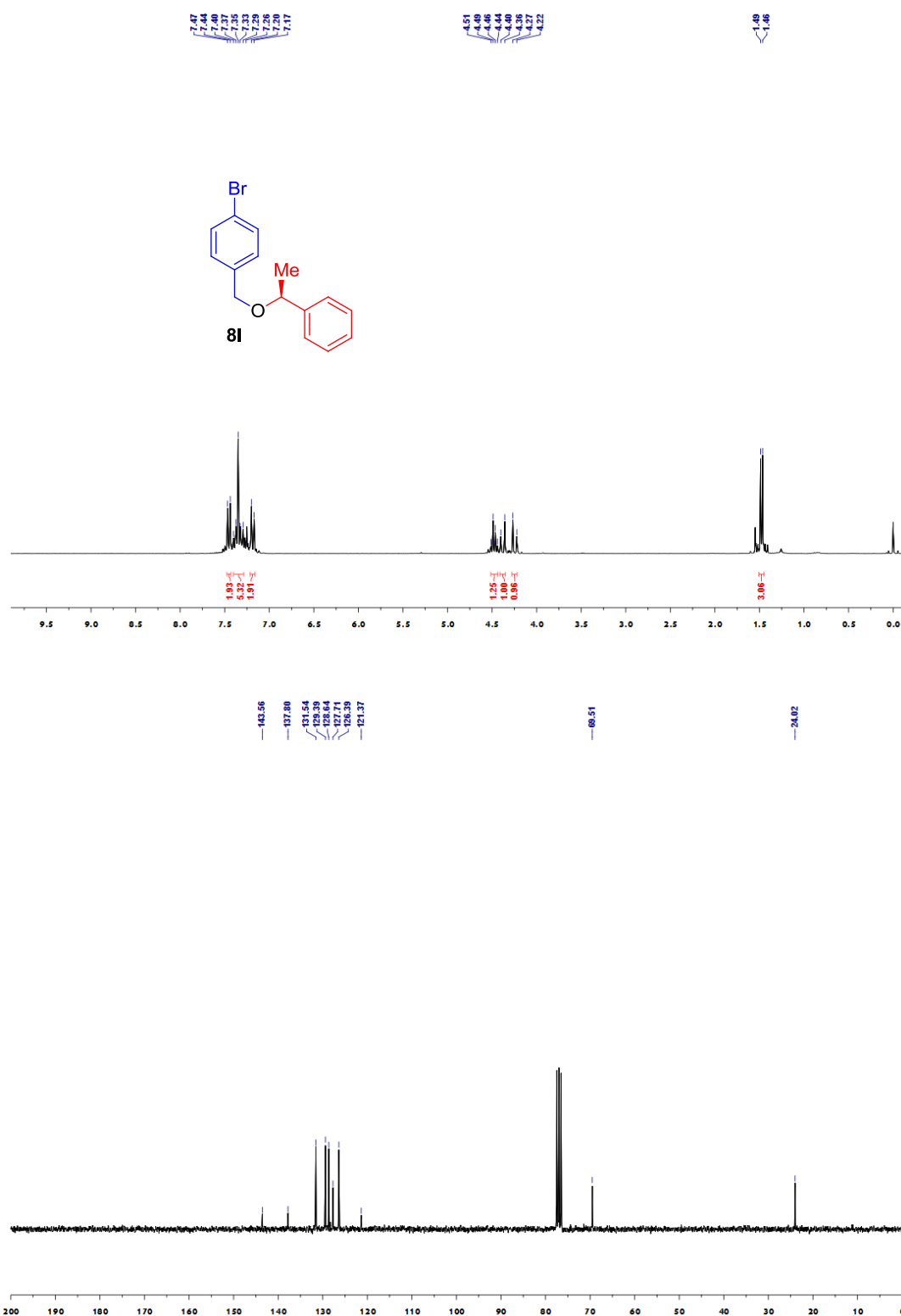


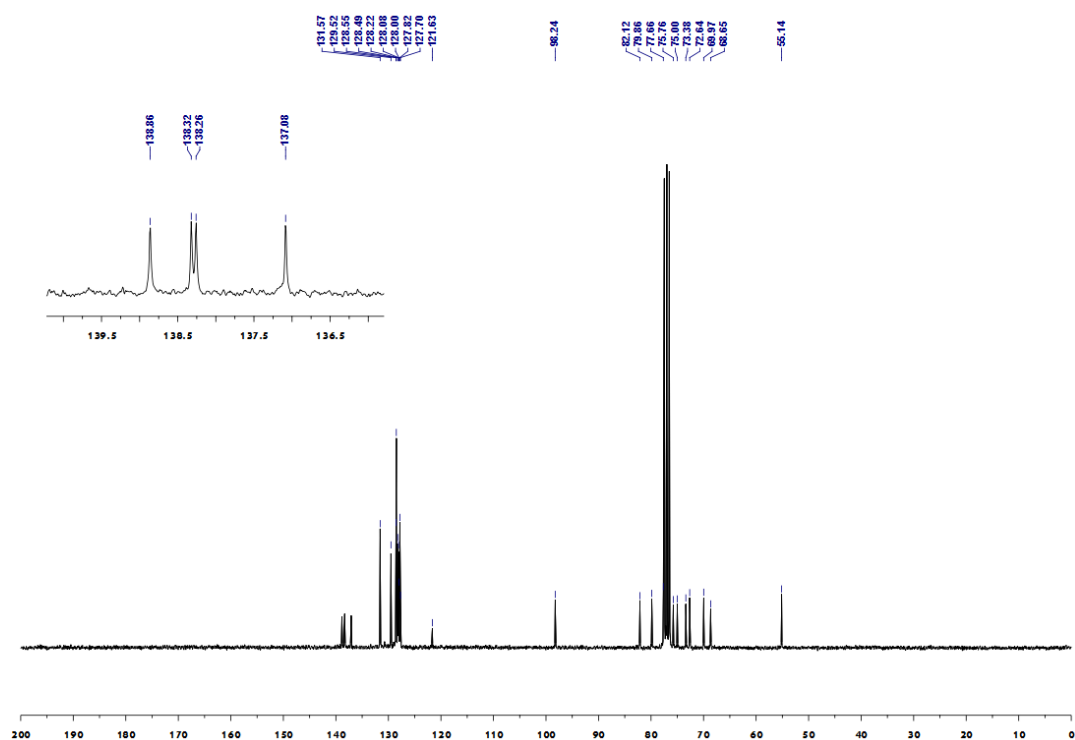
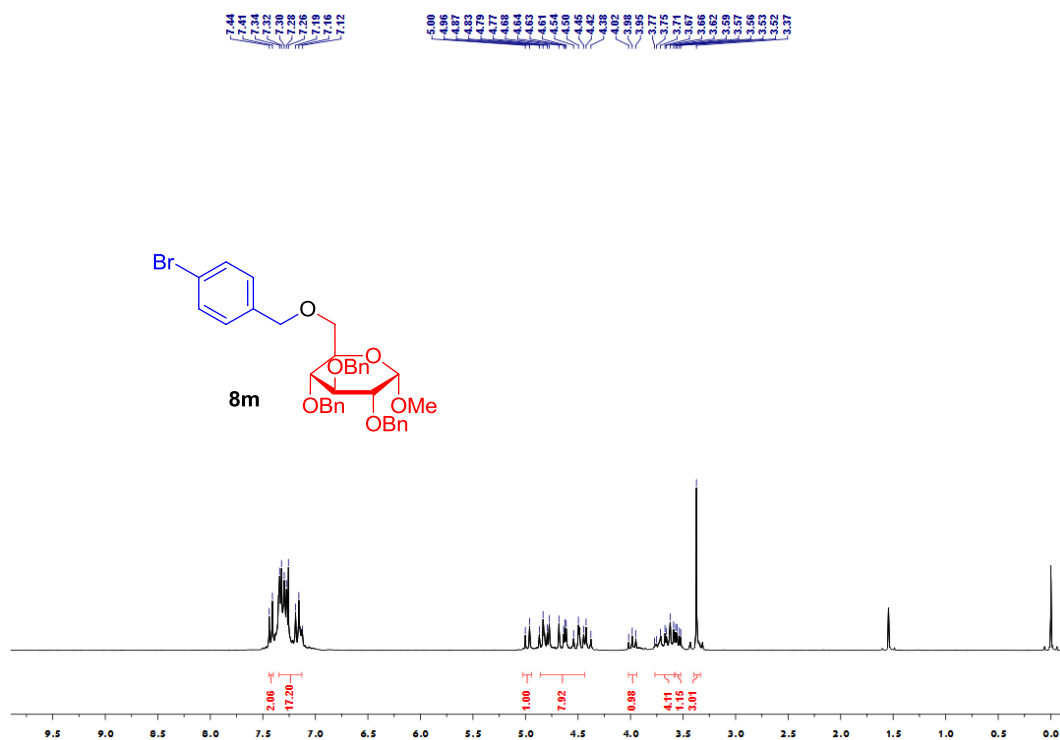


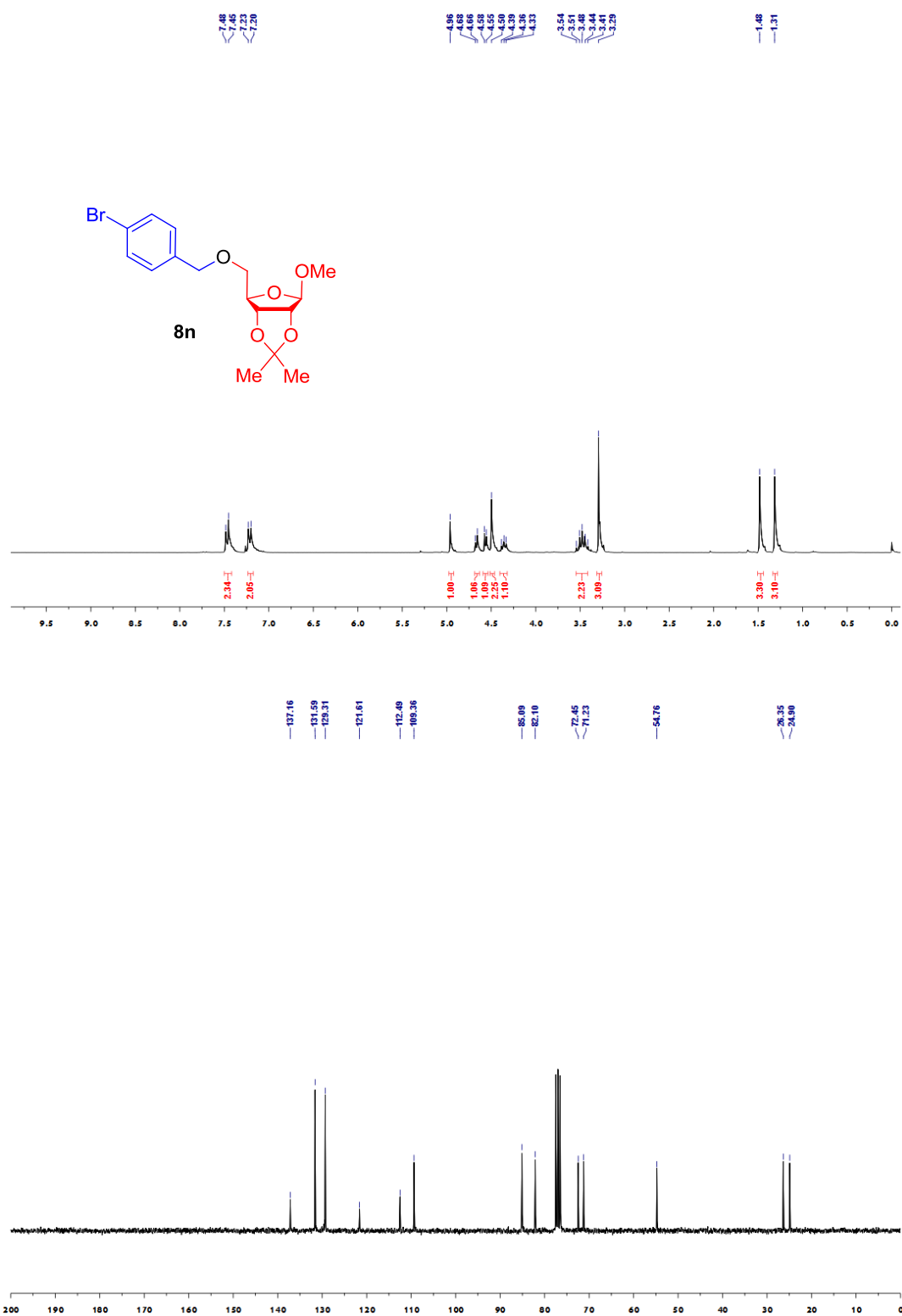


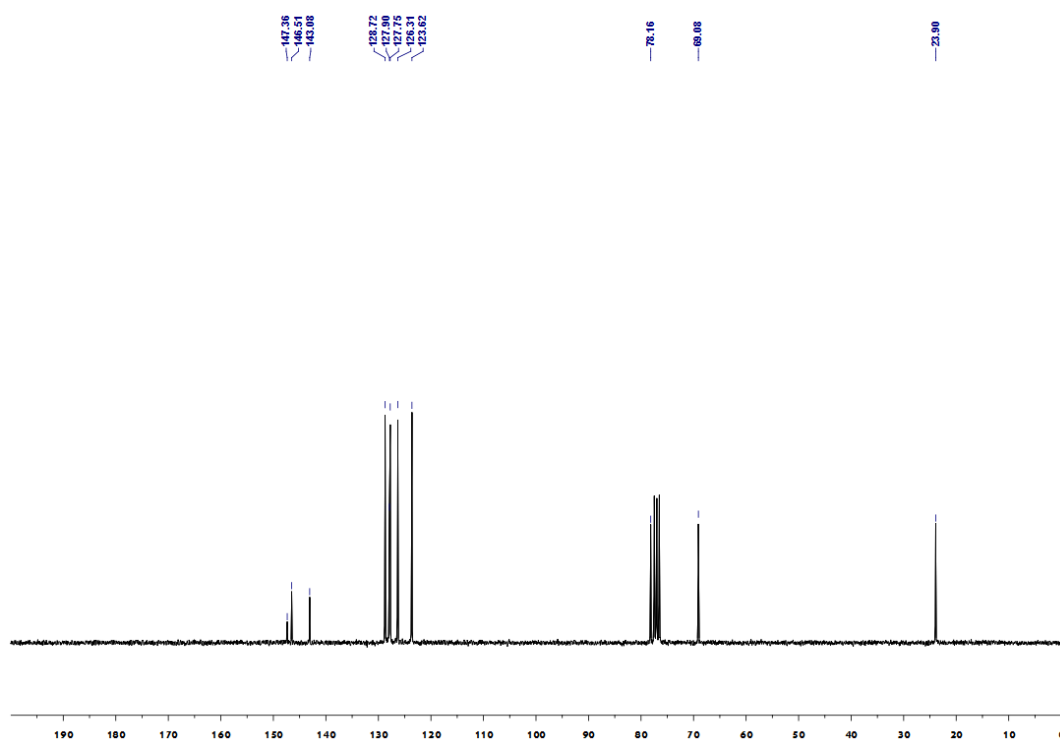
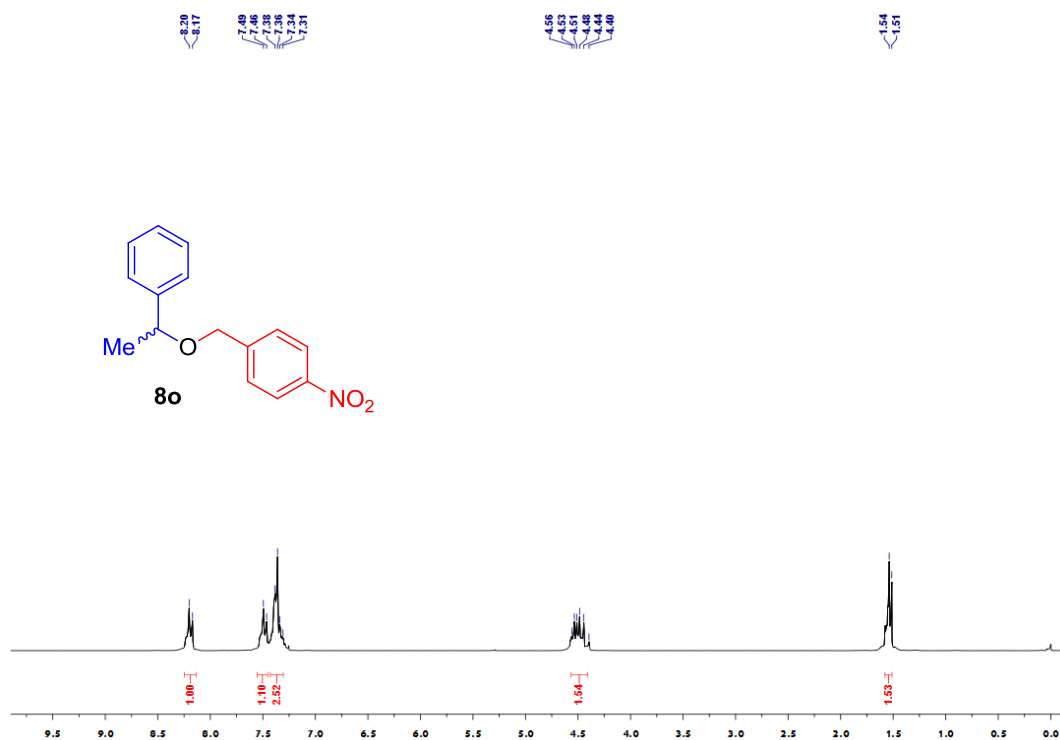


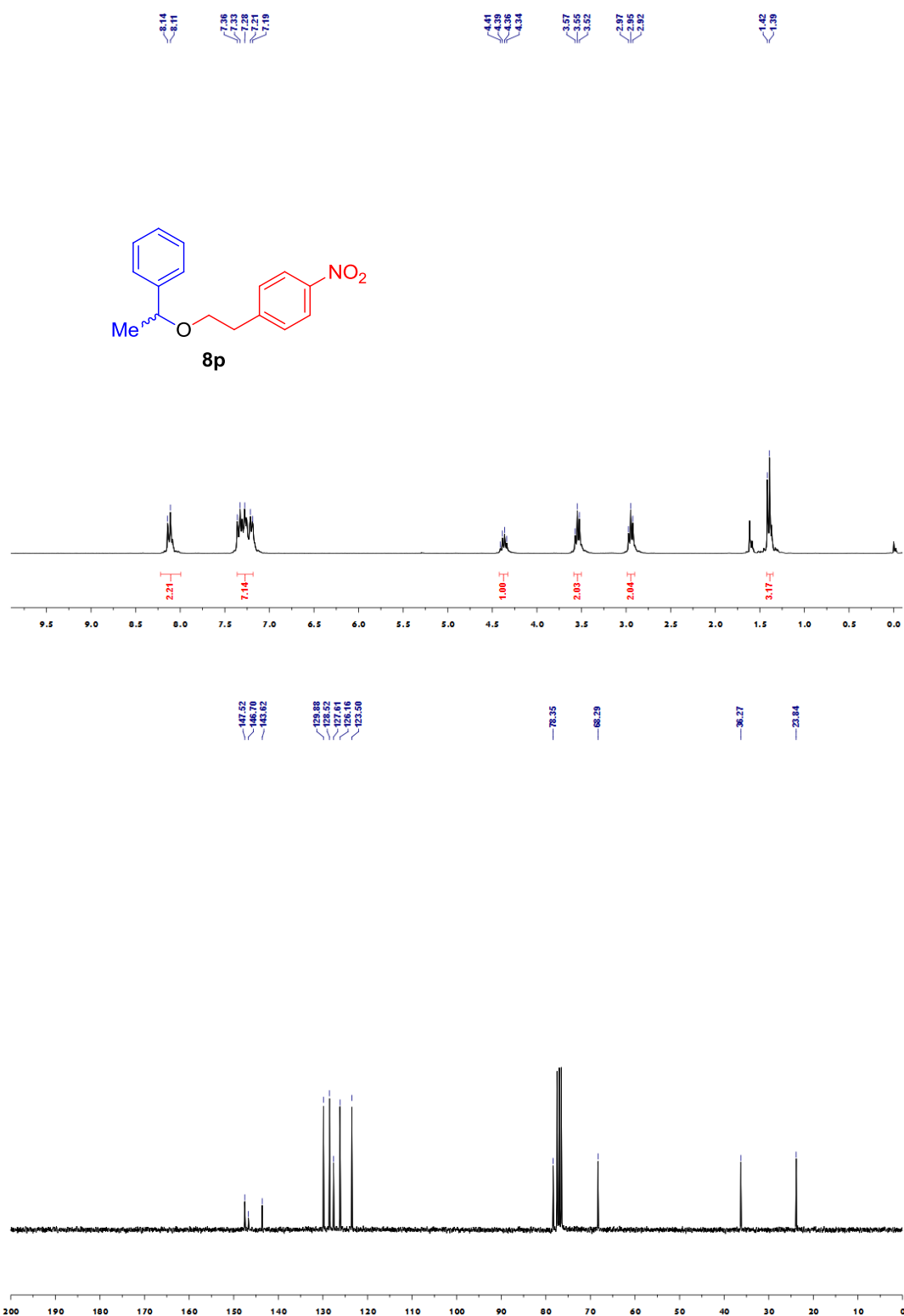




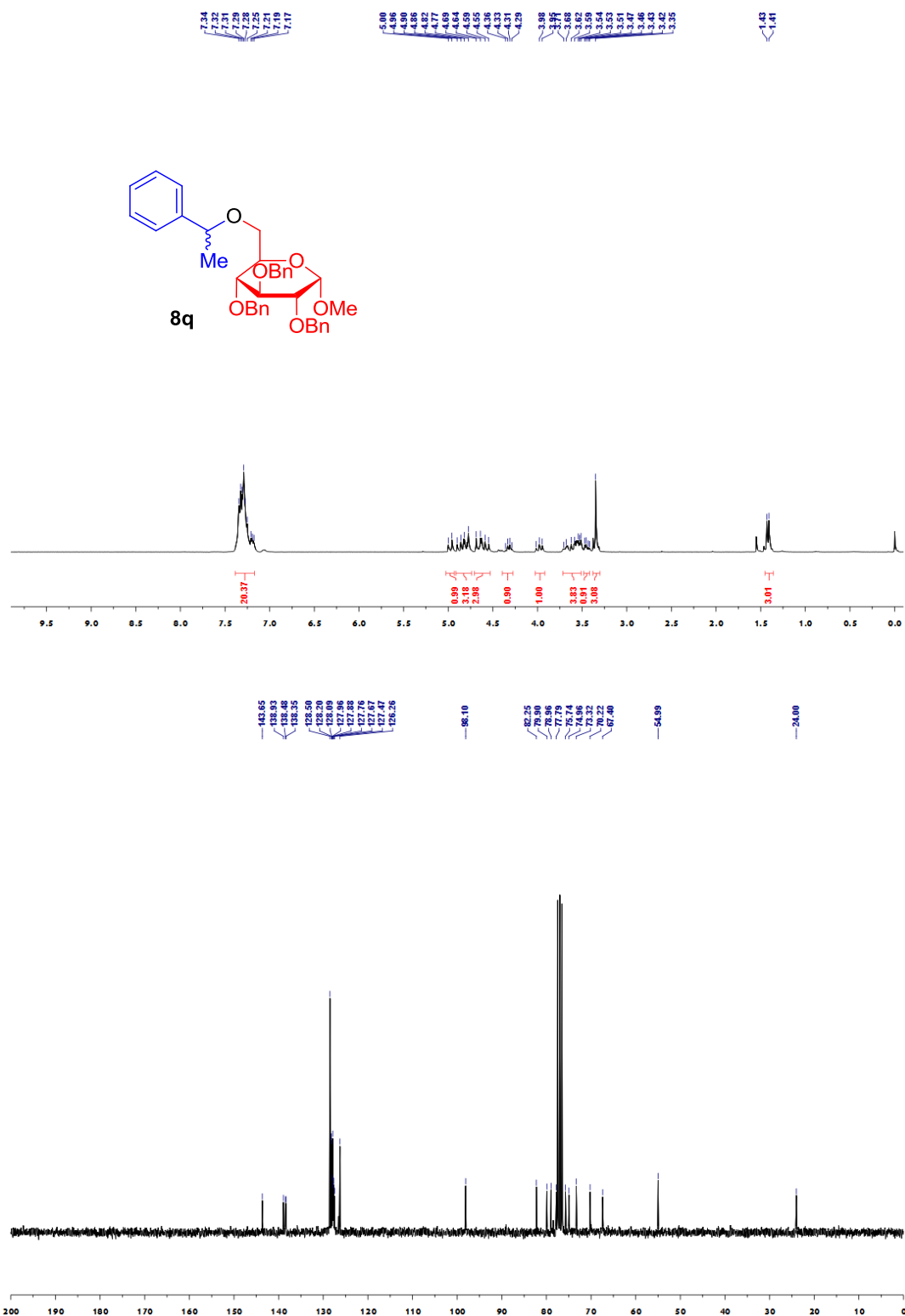


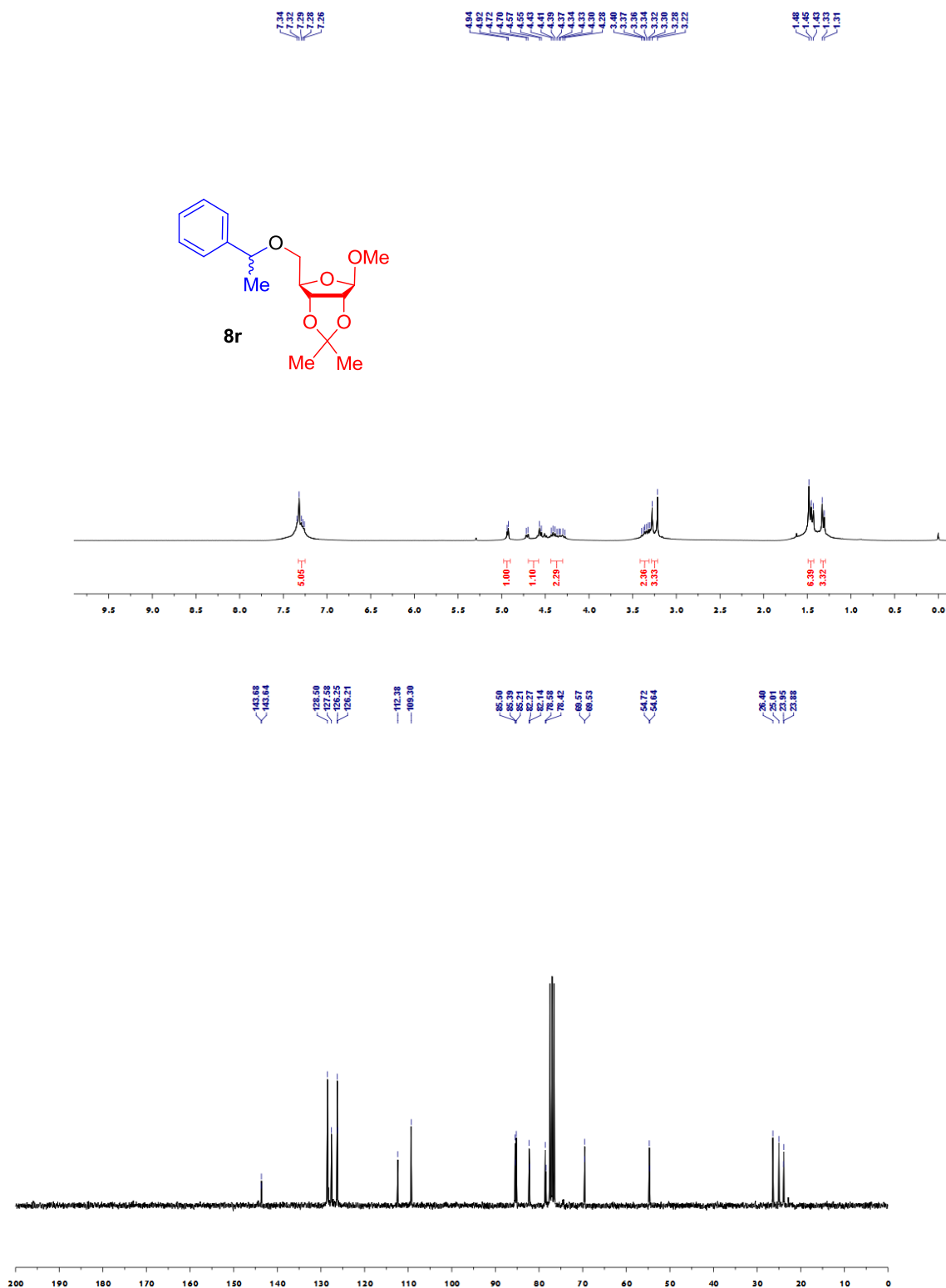


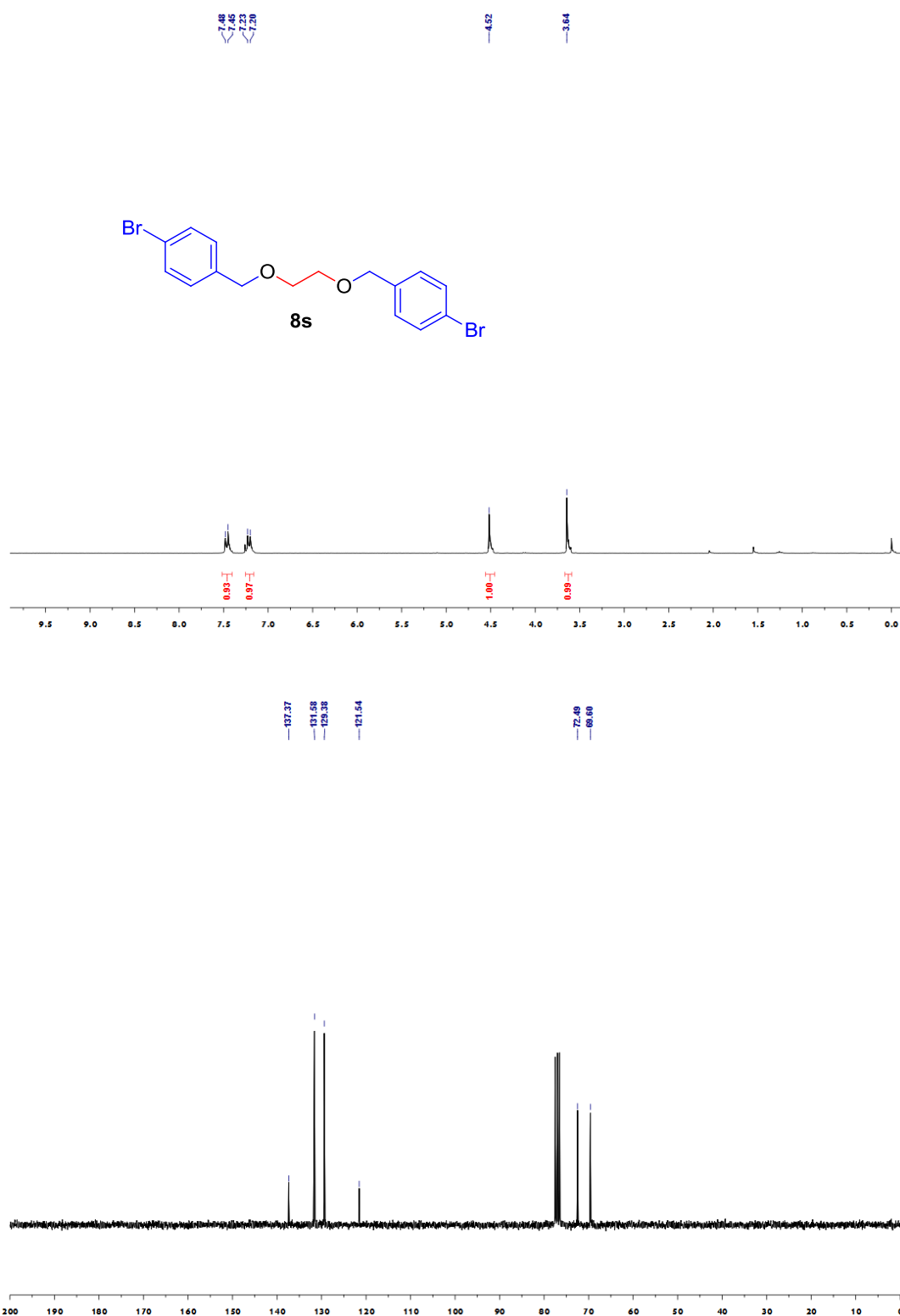


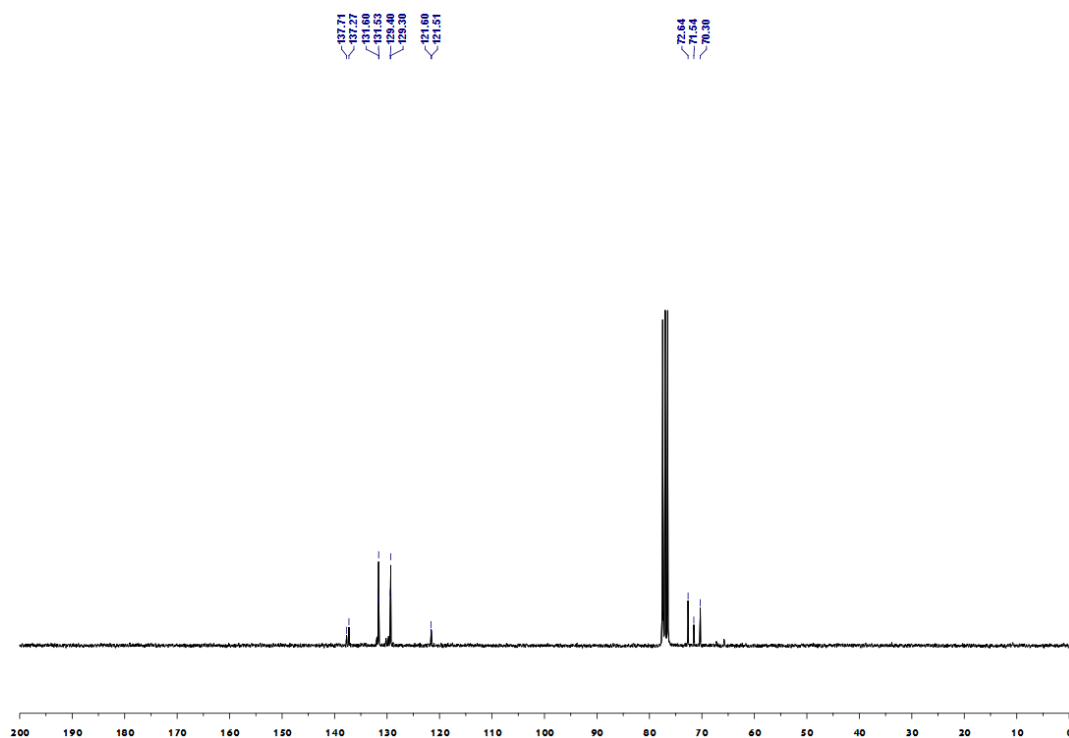
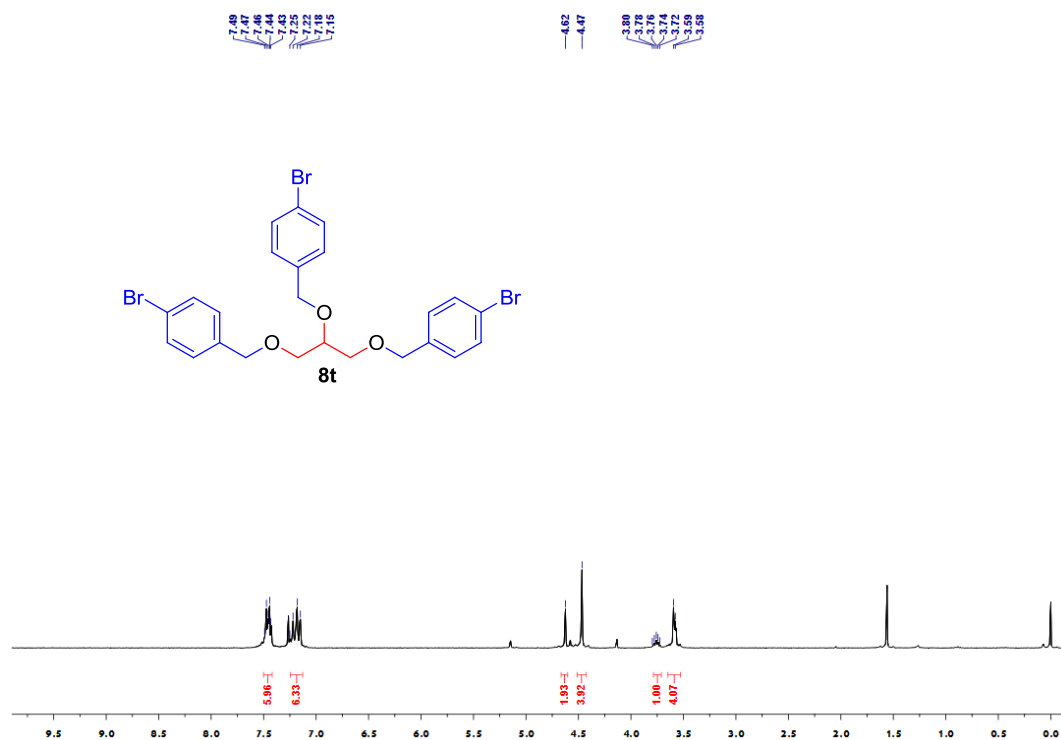


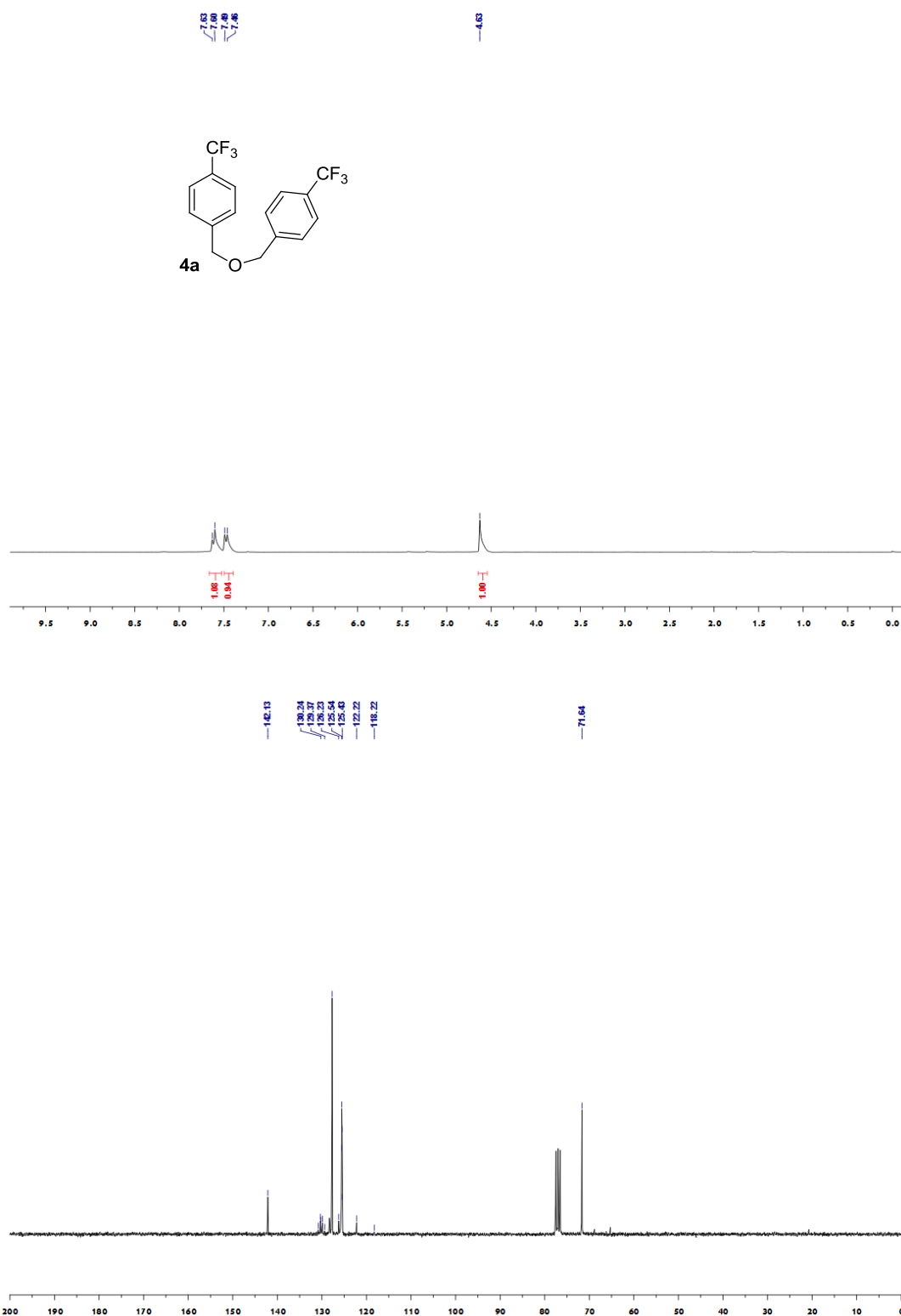




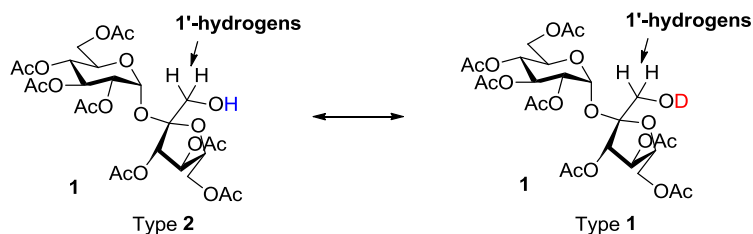




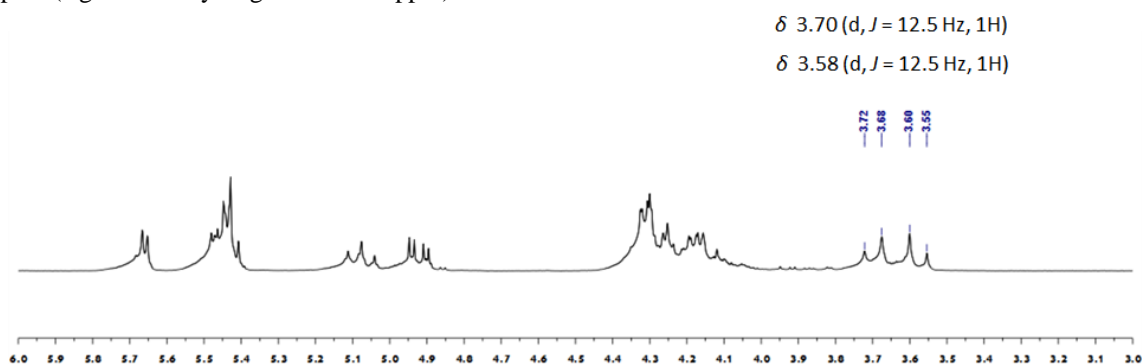




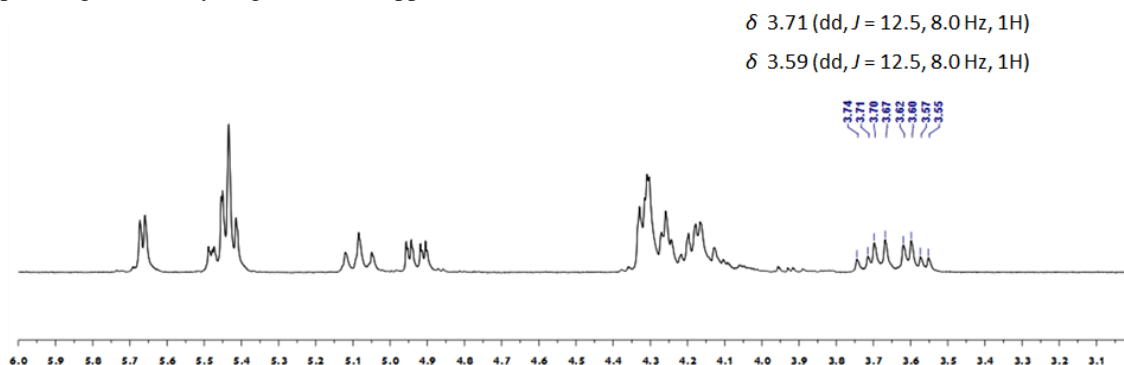
## Two types of $^1\text{H}$ -NMR for 1'-hydrogens of compound **1**



Type **1** (signal of 1'-hydrogens: 3.5-3.8 ppm)



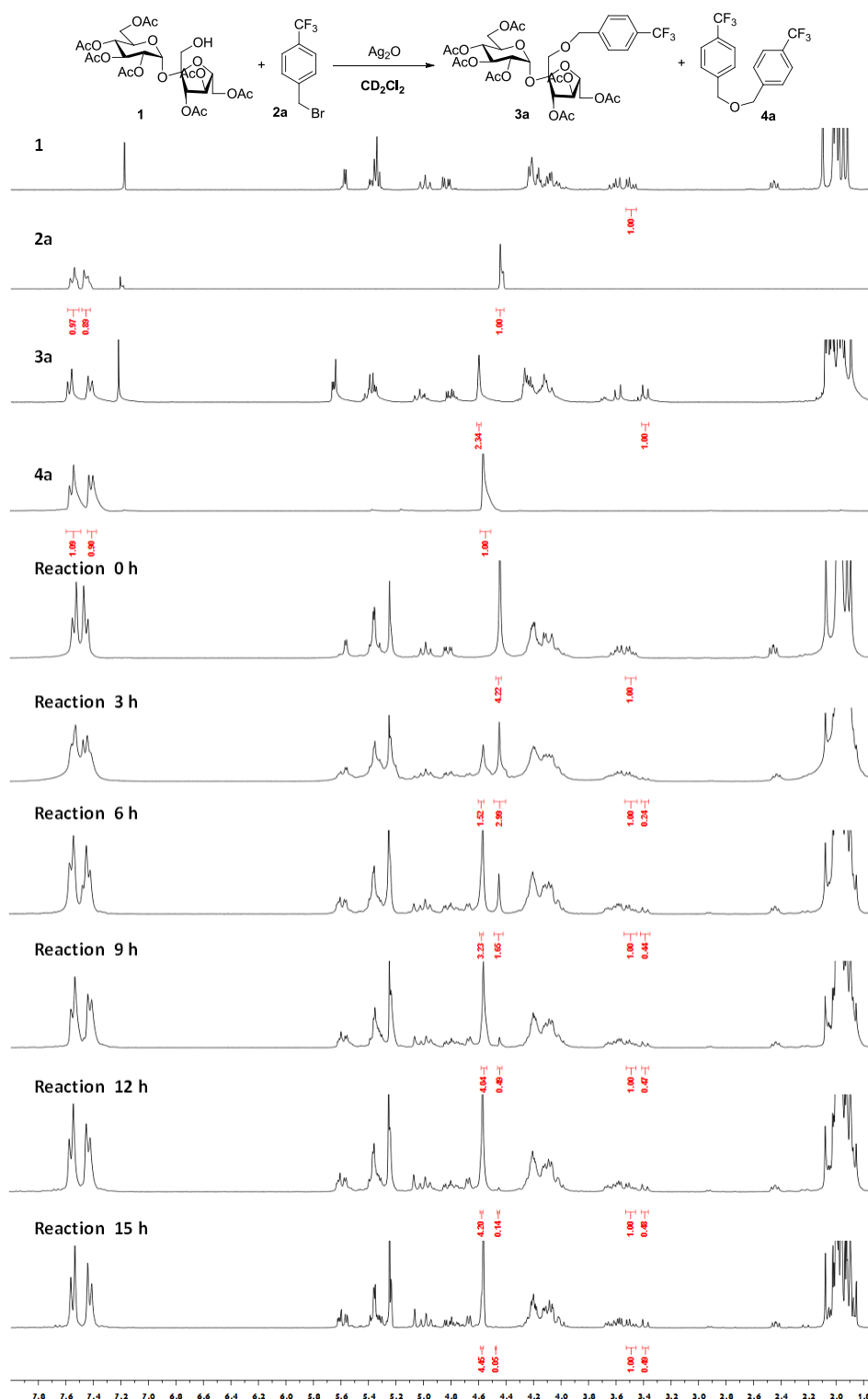
Type **2** (signal of 1'-hydrogens: 3.5-3.8 ppm)

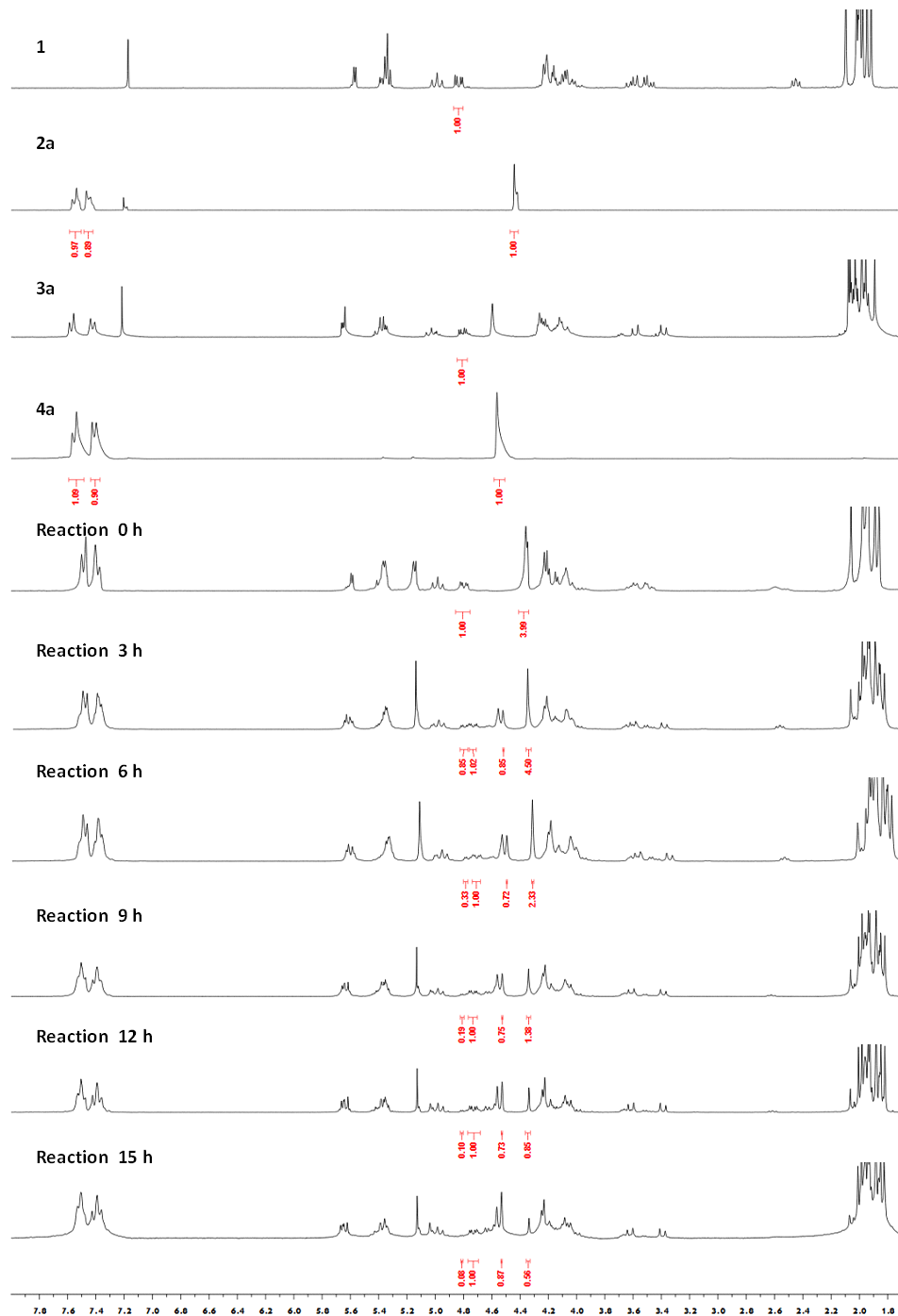
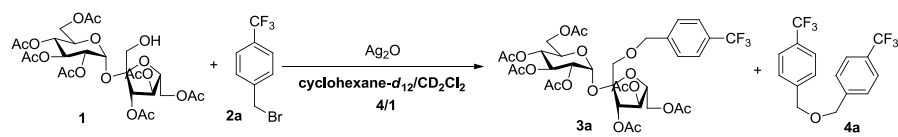


( $^1\text{H}$ -NMR of compound **1**. Chemical shift: 3-6 ppm. Measured in  $\text{CDCl}_3$ )

Previous report (*Carbohydr. Res.* 1991, 222, 121-129) provided the same  $^1\text{H}$ -NMR data as type **1**. While, type **2** was always obtained during the measurement by  $\text{CDCl}_3$  in this study. The difference between type **1** and **2** should be possibly derived from the deuterium exchange occurred at 1'-hydroxyl in the presence of some active proton containing reagents ( $\text{D}_2\text{O}$ , etc) existed in  $\text{CDCl}_3$  or introduced during the measurement. (With the addition of one drop of  $\text{D}_2\text{O}$ , type **2** can be converted to type **1**)

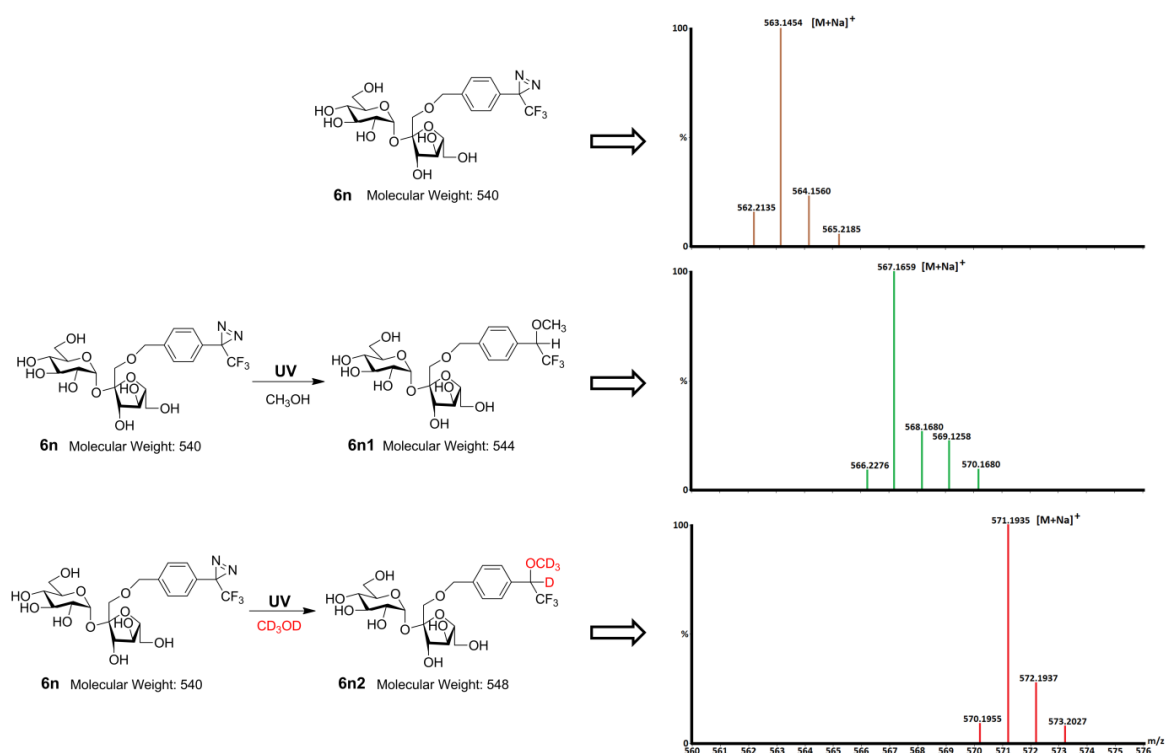
# Kinetic investigation of benzylation of **1** by Ag<sub>2</sub>O in CD<sub>2</sub>Cl<sub>2</sub> and deuterated cosolvent



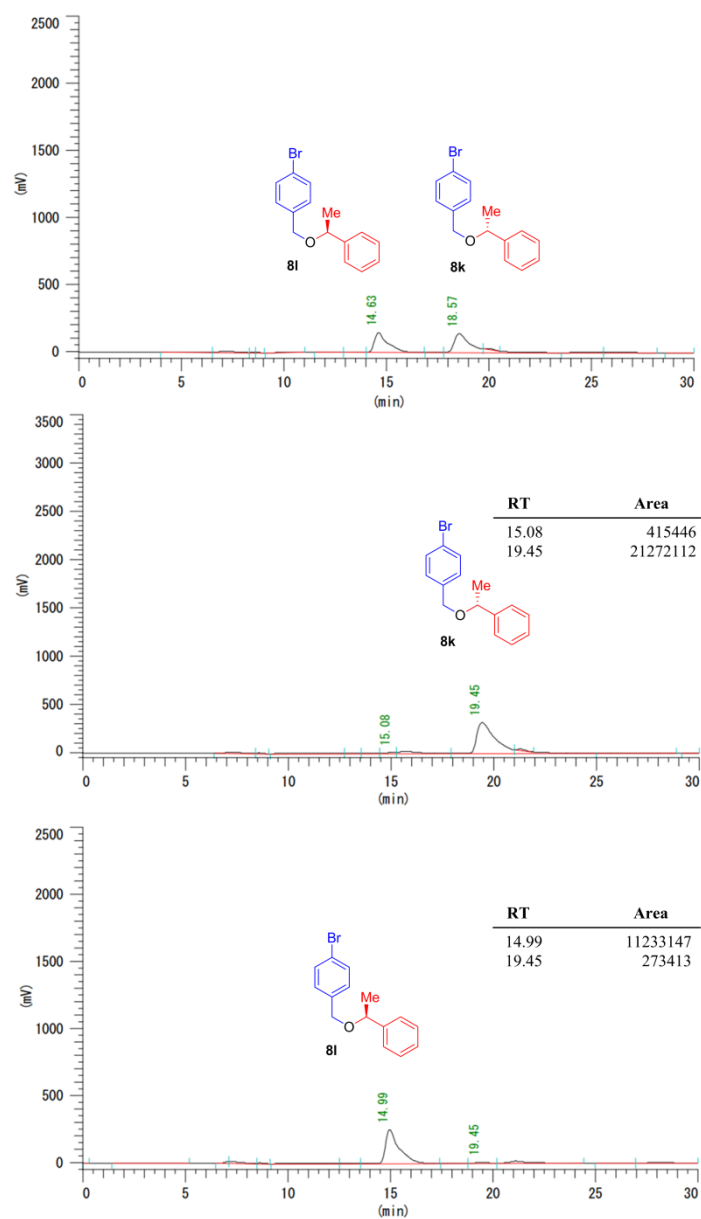




## Mass spectra of 6n after irradiation for 10 min in CH<sub>3</sub>OH or CD<sub>3</sub>OD



## HPLC analysis data for compounds **8k** and **8l**



HPLC (Chiralcel OJ column, *n*-hexane/*i*-PrOH=85:15, 0.5 mL/min, 210 nm),

**8k**:  $t_R(\text{major}) = 19.45$  min,  $t_R(\text{minor}) = 15.08$  min; ee = 96%

**8l**:  $t_R(\text{major}) = 14.99$  min,  $t_R(\text{minor}) = 19.45$  min; ee = 95%